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EC Harmonization Programme for Air Quality Measurements:

The evaluation of the Intercomparison Exercise for SO_2, CO, O_3, NO and NO_2 - June 2007 -

Matej Kapus Dukarić, Annette Borowiak, Fritz Lagler and Michel Gerboles

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Contact information
Address:T.P. 441, Via E. Fermi, 21027 Ispra (VA), Italy
E-mail: annette.borowiak@jrc.ec.europa.eu
Tel.: +39 0332 789956
Fax: +39 0332 785236

http://ies.jrc.ec.europa.eu/
http://www.jrc.ec.europa.eu/

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WHO COLLABORATING CENTRE FOR AIR QUALITY
MANAGEMENT AND AIR POLLUTION CONTROL

at the

FEDERAL ENVIRONMENTAL AGENCY

Executive Summary

In June 2007 in Ispra (IT), 9 AQUILA (Network of European Air Quality Reference Laboratories) laboratories and one laboratory of the World Health Organisations (WHO) Euro-Region met at an intercomparison exercise to evaluate their proficiency in the analysis of inorganic gaseous pollutants covered by European Air Quality Directives (SO_2, CO, NO, NO_2 and O_3).

The proficiency evaluation, where each participant's bias was compared to two criteria, provides information on the current situation and capabilities to the European Commission and can be used by participants in their quality control system.

In terms of criteria imposed by the European Commission, 60% of the results reported by AQUILA laboratories were good both in terms of measured values and reported uncertainties. Another 37% of the results had good measured values, but the reported uncertainties were either too small (4%) or too high (33%).

The comparability of results among AQUILA participants is satisfactory for O_3, SO_2, CO and NO measurement method, but the pollutant NO_2 needs further improvements and harmonization programmes.

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Abbreviations:

AQUILA	Network of National Reference Laboratories for Air Quality
CO	Carbon monoxide
DQO	Data Quality Objective
ERLAP	European Reference Laboratory of Air Pollution
EC	European Commission
GPT	Gas phase titration
IE	Intercomparison Exercise
IES	Institute for Environment and Sustainability
ISO	International Organization for Standardization
JRC	Joint Research Centre
NO	Nitrogen monoxide
NO_2	Nitrogen dioxide
NO_X	the oxides of nitrogen, the sum of NO and NO_2
NRL	National Reference Laboratory
O_3	Ozone
SO_2	Sulphur dioxide
WHO CC	World Health Organization Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin

Mathematical Symbols:

symbol	*explanation*
E_n	E_n – number statistic (ISO 13528; [17])
X	Assigned/reference value (ISO 13528; [17])
u_X	The standard uncertainty of the assigned/reference value (ISO 13528; [17])
U_X	The expended uncertainty of the assigned/reference value (ISO 13528; [17])
x_i	the average of three values reported by the participant i (for particular parameter and concentration level) (ISO 5725; [18])
$x_{i,j}$	j-th reported value of participant i (for particular parameter and concentration level) (ISO 5725; [18])
U_{xi}	The expended uncertainty of the participant's value
z'	z'-score statistic (ISO 13528; [17])
σ_p	the standard deviation for proficiency assessment (ISO 13528; [17])
x*	robust average (Annex C ISO 13528; [17])
s*	robust standard deviation (Annex C ISO 13528; [17])
α	converter efficiency (EN 14211; [8])
s_r	repeatability standard deviation (ISO 5725; [18])
s_R	reproducibility standard deviation (ISO 5725; [18])
r	repeatability limit (ISO 5725; [18])
R	reproducibility limit (ISO 5725; [18])

1. Introduction

The Framework Directive 96/62/EC [1] on Ambient Air Quality Assessment and Management sets up a framework for a harmonized air quality assessment in Europe. One important objective of this Directive is that the ambient air quality shall be assessed on the basis of common methods and criteria. The first “Daughter Directive” [2] deals with the air pollutants sulphur dioxide (SO_2), nitrogen dioxide (NO_2) and monoxide (NO), particulate matter and lead. Among others it specifies the reference methods for measurements and Data Quality Objectives (DQO) for the accuracy of measurements. The second “Daughter Directive” [3], dealing with benzene and carbon monoxide (CO), the third one [4] dealing with ozone (O_3), and the fourth one [5], dealing with heavy metals and polycyclic aromatic hydrocarbons, establish target values, the DQOs and reference methods for the mentioned compounds as well. In June 2008 the Framework Directive and her first three daughters have been replaced by the CAFÉ Directive 2008/50/EC. Data Quality Objectives and the reference methods remained unchanged for the pollutants of interest.

The European Commission (EC) has supported the development and publication of reference measurement methods [6], [7], [8] and [9] as European standards. Appropriate calibration methods [10], [11] and [12] have been standardised by the International Organization for Standardization (ISO).

As foreseen in the Framework Directive, the European Reference Laboratory of Air Pollution (ERLAP) of the Institute for Environment and Sustainability (IES) at the Joint Research Centre (JRC) organizes intercomparison exercises (IE) to assess and improve the status of comparability of measurements of National Reference Laboratories (NRL) of each Member State of the European Union.

The World Health Organization Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin (WHO CC) is carrying out similar activities since 1994 [13] [14], but with a view to obtaining harmonized air quality data for health related studies. Their program integrates within the WHO EURO region, which includes public health institutes and other national institutes - especially from the Central Eastern Europe, Caucasus and countries from Central Asia.

Starting in 2004, it has been decided to bring together the efforts of both the JRC-ERLAP and WHO CC and to coordinate activities as far as possible, with a view to optimize resources and have better international harmonization. The following report deals with the IE that took place from the 4th to the 7th of June 2007 in Ispra (IT) in joint cooperation of EC/ JRC/IES/ERLAP and WHO CC-EURO.

ERLAP has been organizing IEs since 1990 aiming at evaluating the comparability of measurements carried out by NRLs and promoting information exchange among the expert laboratories. Nowadays the main objective, in accordance with the Network of National Reference Laboratories for Air Quality (AQUILA) [15], comprises a more systematic approach that offers alert mechanism for the purposes of the EC and is also useful to NRLs in quality assurance of their implemented quality systems. The methodology of organization of IEs was developed by ERLAP and is described in a position paper on the organization of intercomparison exercises for gaseous air pollutants [16]. This position paper is currently a proposal to the AQUILA and the final agreement of position paper is foreseen to take place during 2008. Then it will be applied throughout all future IEs.

The evaluation scheme applied to this IE is described in detail in the position paper [16] and it reflects the inputs given by AQUILA. Firstly, it was acknowledged that the evaluation scheme should have common criteria, to alert the EC on the possible performance failure, and not to base these alerts on claimed uncertainty of participants. For that purpose the common criterion was proposed to AQUILA and the z’-score method [17] was implemented in to the evaluation scheme. The common criterion is derived from the uncertainty requirements for calibration gases stated in the European standards [6], [7], [8] and [9], which are consistent with the DQOs of European Directives. In view of AQUILA, NRLs with overall unsatisfactory results of the z'-score evaluation (one unsatisfactory or two questionable results per parameter) are required to repeat their participation to the next IE in order to demonstrate remediation measures [16]. Secondly, it was acknowledged that the evaluation scheme should be useful to participants accredited according to ISO 17025 and thus should include measurement uncertainty of participants. For that purpose, participants measurement results (measurement values and uncertainties) are compared to assigned values applying the E_n – number method [17].

Beside the proficiency of participating laboratories the repeatability and reproducibility of standardized measurement methods [18], [19] and [20] are evaluated as well. These group evaluations will be used in a separate communication as the indicators of trends of quality of measurements over different IEs undertaken by ERLAP.

2. Communication and time schedule

The IE was announced in November 2006 to the members of the AQUILA network and the WHO CC representative. A registration letter was sent to interested parties and the registration was closed in April 2007 with the full list of 11 participating laboratories. The participants were required to bring their own measurement instruments, data acquisition equipment and travelling standards (to be used for calibrations or checks during the IE).

The participants were invited to arrive on Monday, 4th June 2007, for the installation of their equipment. The calibration of NOx and O_3 analysers was carried out on Tuesday morning and the generation of NOx and O_3 gas mixtures started at 11:00. The calibration of SO_2 and CO analysers was carried out on Wednesday 18:00 and the generation of CO and SO_2 gas mixtures started at 20:00. The test gases generation finished on Thursday at 7:00 a.m..

3. Participants

The majority of participants were organizations dealing with the routine ambient air quality monitoring on the national levels of EU member states. The representatives came from Bulgaria, Czech Republic, Estonia, Ireland, Poland, Slovenia, Spain and United Kingdom. In addition the Czech National Institute of Public Health is involved in health related studies and GAW EMEP station is operated by the EC/ JRC/IES/ ‘Climate Change Unit – Global Air Pollution and Climate Change action’

Table 1: The list of participating organizations.

Country	Name of Organization	IE code
Bulgaria	Executive Environmental Agency	A
Czech Republic	Czech Hydrometeorological Institute	B
Czech Republic	National Institute of Public Health	C
Estonia	Estonian Environmental Research Centre	D
European Commission	European reference laboratory for air polution	E
European Commission	GAW EMEP super site	F
Ireland	Environmental Protection Agency	G
Poland	Voivodshi Inspectorate for Environment Protecton	H
Slovenia	Environmental Agency of Republic of Slovenia	I
Spain	Ministerio de Medio Ambiente	J
United Kingdom	AEA Technology	K

4. Preparation of test mixtures

The ERLAP IE facility has been described in several reports [21] and [22]. During this IE, gas mixtures were prepared for SO_2, CO, O_3, NO and NO_2 at concentration levels around the European Air Quality limit values, critical levels and assessment thresholds.

The test mixtures were prepared by the dilution of gases from cylinders containing high concentration of NO, SO_2 or CO using thermal mass flow controllers [12]. O_3 was added using an ozone generator and NO_2 was produced applying the gas phase titration method [23] in the conditions of excess NO.

The participants were required to report three half-hour-mean measurements for each concentration level in order to evaluate the repeatabilities of standardized measurement methods. Zero concentration levels were generated for one hour and one half-hour-mean measurement was reported. In Table 2, the sequence program of generated test gases – 'target values' is given.

Table 2: The sequence program of generated test gases – target values

day	start time	duration	operation or run number	zero air	NO	NO_2	O_3	CO	SO_2
		(h)		(nmol/mol)	(nmol/mol)	(nmol/mol)	(nmol/mol)	(µmol/mol)	(nmol/mol)
04-Jun	12:00	6	installation						
05-Jun	08:00	3	calibration						
05-Jun	11:00	1	NO & NO_2 & O_3 run 0	0					
05-Jun	12:00	2	NO & NO_2 run 1		500	0			
05-Jun	14:00	2	NO & NO_2 run 2		380	120			
05-Jun	16:00	2	O_3 run 1				120		
05-Jun	18:00	2	NO & NO_2 run 3		250	0			
05-Jun	20:00	2	NO & NO_2 run 4		146	104			
05-Jun	22:00	2	O_3 run 2				104		
06-Jun	00:00	2	NO & NO_2 run 5		150	0			
06-Jun	02:00	2	NO & NO_2 run 6		90	60			
06-Jun	04:00	2	O_3 run 3				60		
06-Jun	06:00	2	NO & NO_2 run 7		50	0			
06-Jun	08:00	2	NO & NO_2 run 8		29.1	20.9			
06-Jun	10:00	2	O_3 run 4				20.9		
06-Jun	12:00	2	NO & NO_2 run 9		15.7	0			
06-Jun	14:00	2	NO & NO_2 run 10		2.1	13.6			
06-Jun	16:00	2	O_3 run 5				13.6		
06-Jun	< 18:00	2	calibration						
06-Jun	20:00	1	CO & SO_2 run 0	0					
06-Jun	21:00	2:30	CO & SO_2 run 1					8.6	132
06-Jun	23:30	2	CO & SO_2 run 2					6	47
07-Jun	01:30	2	CO & SO_2 run 3					4.3	18.8
07-Jun	03:30	2	CO & SO_2 run 4					2	7.5
07-Jun	05:30	2	CO & SO_2 run 5					1	3
07-Jun	07:30	1		0					

5. Evaluation of laboratory's measurement proficiency

To evaluate the participants measurement proficiency the methodology described in ISO 13528 [17] was applied. It has been agreed among the members of the AQUILA to take the measurement results of ERLAP as the assigned/reference values for the whole IE [16]. The traceability of ERLAP's measurement results and the method applied to validate them are presented in Annex A. In the following proficiency evaluations, the uncertainty of test gas homogeneity (Annex A) was added to the uncertainties of ERLAP's measurement results.

All data reported by participating laboratories are presented in Annex B.

As it is described in the position paper [16], the proficiency of the participants was assessed by calculating two performance indicators. The first performance indicator (z'-score) tests if the difference between the participants measured value and the assigned/reference value remains within the limits of a common criterion, while the second performance indicator (E_n-number) tests if the difference between the participants measured values and assigned/reference value remains within the limits of a criterion, that is calculated individually for each participant, from the uncertainty of the participants measurement result and the uncertainty of the assigned/reference value.

z' - score

The z'- score statistic is calculated according to ISO 13528 [17] as:

$$z' = \frac{x_i - X}{\sqrt{\sigma_p^2 + u_X^2}} = \frac{x_i - X}{\sqrt{(a \cdot X + b)^2 + u_X^2}} \qquad (1)$$

where 'x_i' is a participant's run average value, 'X' is the assigned/reference value, 'σ_p' is the 'standard deviation for proficiency assessment' and 'u_X' is the standard uncertainty of assigned value. For 'a' and 'b' see Table 3.

In the European standards [6], [7], [8] and [9] the uncertainties for calibration gases used in ongoing quality control are prescribed. In fact, it is stated that the maximum permitted expanded uncertainty for calibration gases is 5% and that 'zero gas' shall not give instrument reading higher than the detection limit. As one of the tasks of NRLs is to verify the accuracy of above mentioned 'zero gas' and calibration gas mixtures, the 'standard deviation for proficiency assessment' (σ_p) [17] is calculated in fitness-for-purpose manner from requirements given in European standards.

Over the whole measurement range σ_p is calculated by linear interpolation between 2.5 % at the calibration point (75% of calibration range) and the limit of detection at zero concentration level. The limits of detection of studied measurement methods were evaluated from the data of previous IEs [24]. The linear function parameters of σ_p are given in Table 3.

Table 3: The standard deviation for proficiency assessment as a linear function of concentration (c) with linear function parameters: slope (a) and intercept (b).

	σ_p=a·c+b	
	a	b
		nmol/mol
SO2	0.024	0.4
CO	0.023	100
O3	0.022	0.5
NO	0.025	0.35
NO2	0.023	0.46

During the November 2008 AQUILA meeting, σ_p was enlarged, to 1 ppb at zero concentration of SO_2, O_3, NO, NO_2, and approved. It has been agreed that this change is noted in all relevant and not yet published IE reports and applied to all future IEs.

The z'-score evaluation allows the following criteria to be used for the assessment of results:

- $|z'| \leq 2$ are designated satisfactory.
- $2 < |z'| \leq 3$ are designated questionable.
- $|z'| > 3$ are designated unsatisfactory. Scores falling in this range are very unusual and are taken to indicate that the cause of the event should be investigated and remedied.

The results of z'-score evaluation are presented in bar plots (Figure 1 to Figure 5) in which the z'-scores of each participant are grouped together, and assessment criteria are presented as z'=±2 and z'=±3 lines.

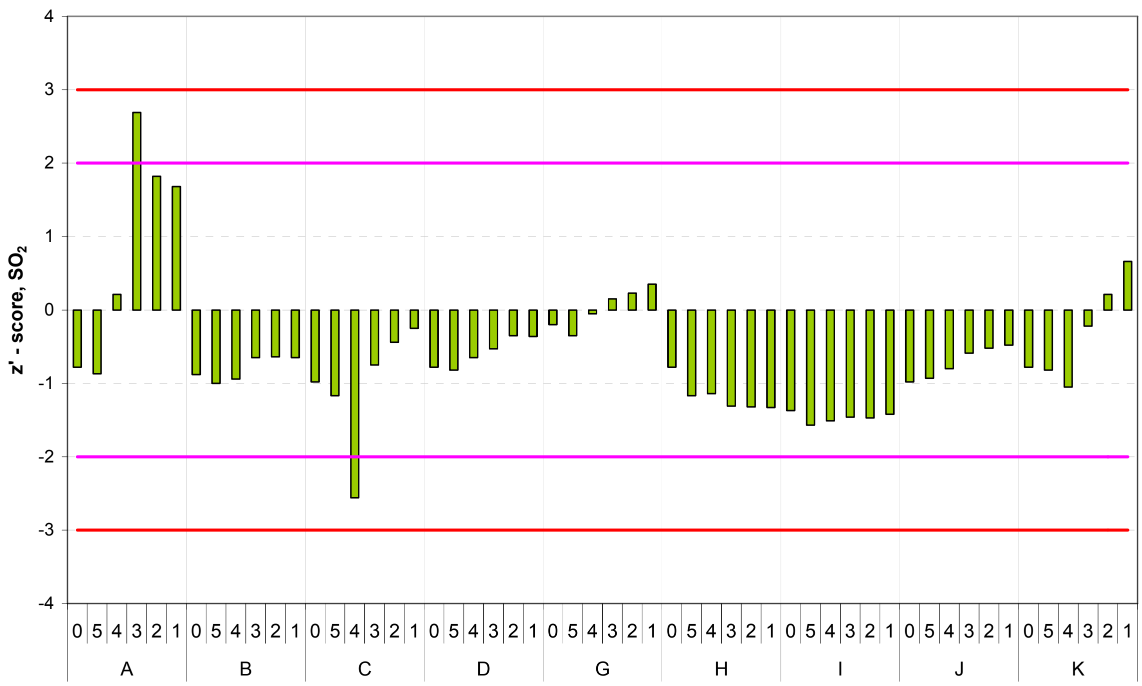

Figure 1: The z'-score evaluations of SO_2 measurements
are given for each participant and each tested concentration level. The evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 nmol/mol), 5 (3 nmol/mol), 4 (7 nmol/mol), 3 (19 nmol/mol), 2 (47 nmol/mol), 1 (132 nmol/mol)). The assessment criteria are presented as z'=±2 and z'=±3 lines. They represent the limits for the questionable and unsatisfactory results.

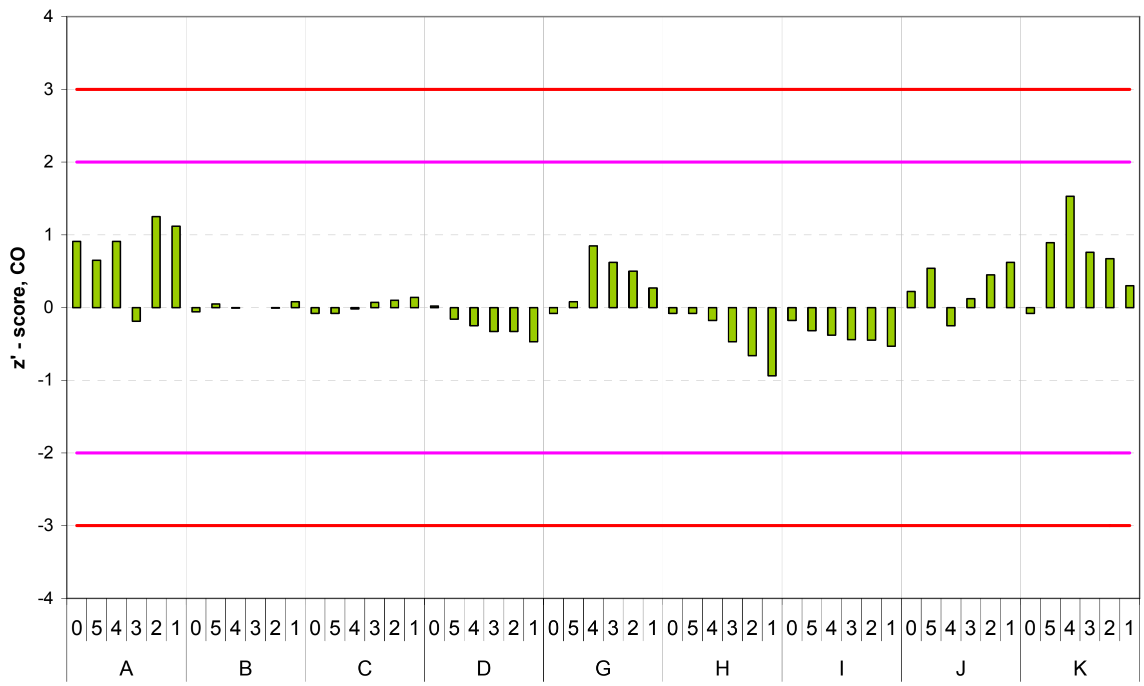

Figure 2: The z'-score evaluations of CO measurements
are given for each participant and each tested concentration level. The evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 µmol/mol), 5 (1 µmol/mol), 4 (2 µmol/mol), 3 (4 µmol/mol), 2 (6 µmol/mol), 1 (9 µmol/mol)). The assessment criteria are presented as z'=±2 and z'=±3 lines. They represent the limits for the questionable and unsatisfactory results.

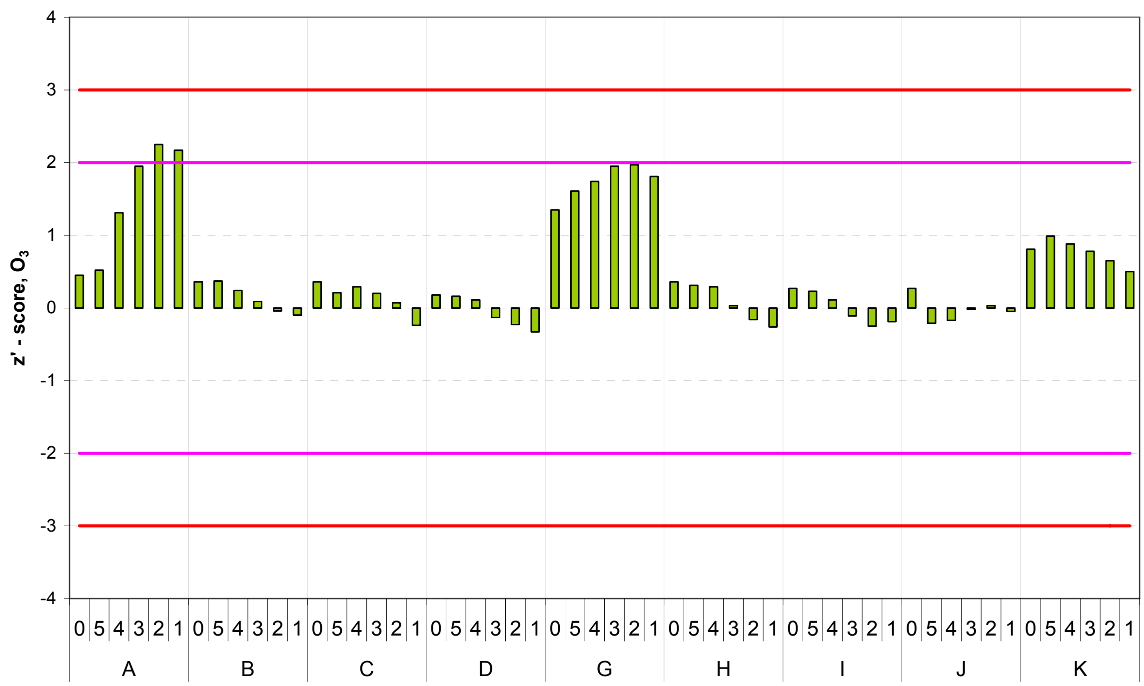

Figure 3: The z'-score evaluations of O_3 measurements
are given for each participant and each tested concentration level. The evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 nmol/mol), 5 (14 nmol/mol), 4 (21 nmol/mol), 3 (60 nmol/mol), 2 (104 nmol/mol), 1 (120 nmol/mol)). The assessment criteria are presented as z'=±2 and z'=±3 lines. They represent the limits for the questionable and unsatisfactory results.

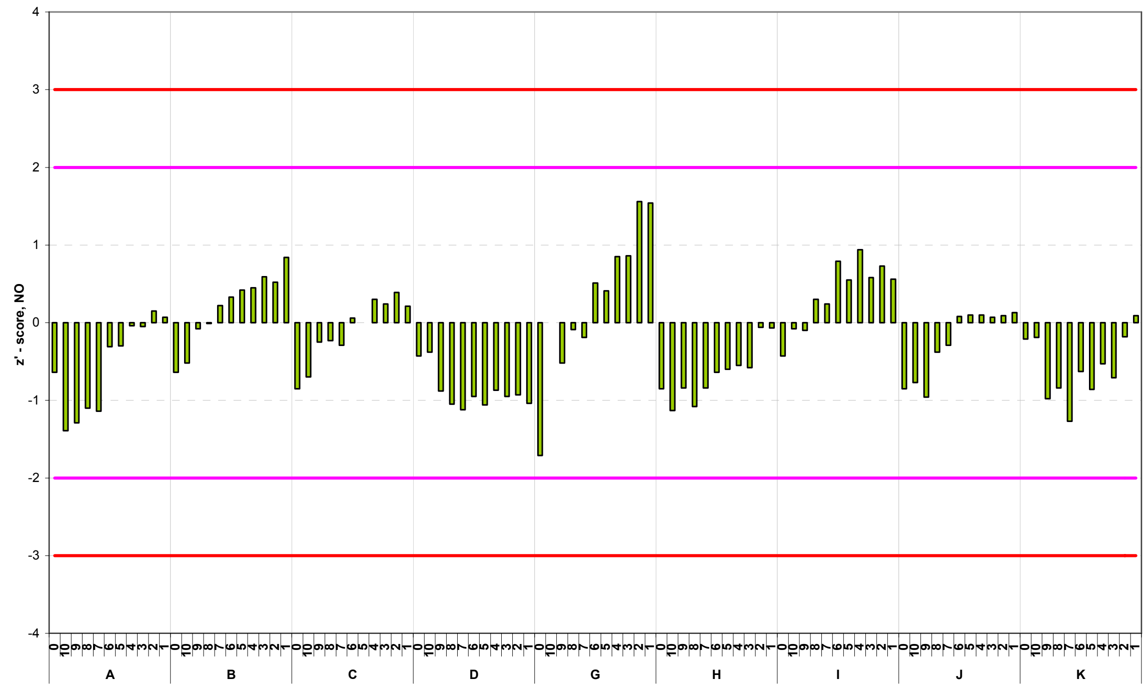

Figure 4: The z'-score evaluations of NO measurements
are given for each participant and each tested concentration level. The evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 nmol/mol), 10 (2 nmol/mol), 9 (16 nmol/mol), 8 (30 nmol/mol), 7 (50 nmol/mol) , 6 (90 nmol/mol) , 5 (150 nmol/mol) , 4 (150 nmol/mol) , 3 (250 nmol/mol) , 2 (380 nmol/mol), 1 (500 nmol/mol)). The assessment criteria are presented as z'=±2 and z'=±3 lines. They represent the limits for the questionable and unsatisfactory results.

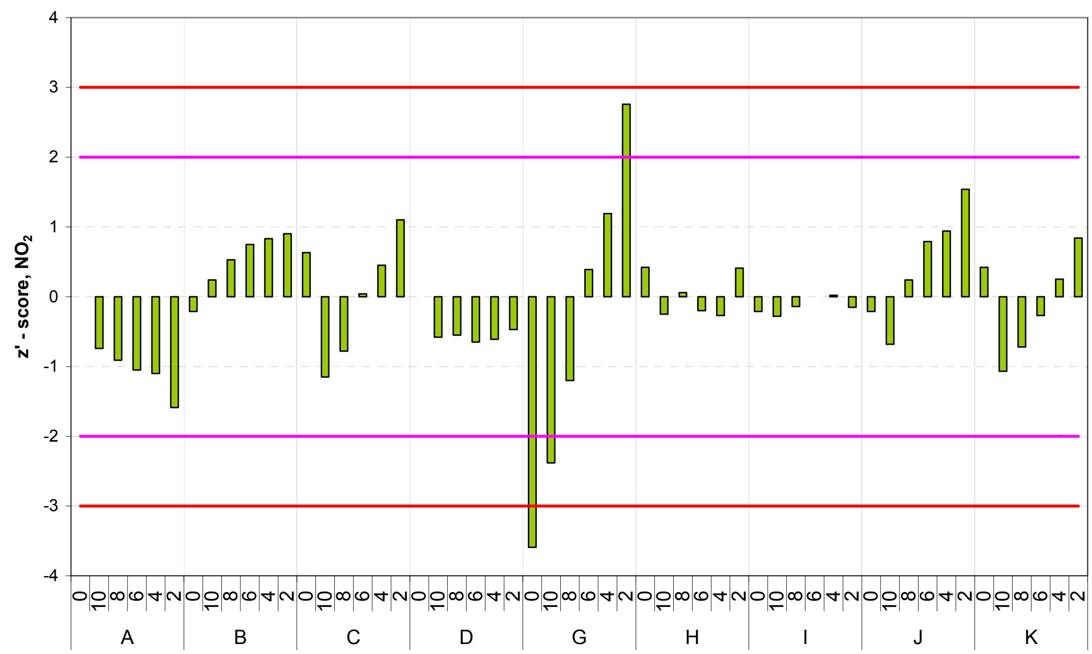

Figure 5: The z'-score evaluations of NO_2 measurements
are given for each participant and each tested concentration level. The evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 nmol/mol), 10 (14 nmol/mol), 8 (21 nmol/mol), 6 (60 nmol/mol), 4 (104 nmol/mol), 2 (120 nmol/mol)). The assessment criteria are presented as z'=±2 and z'=±3 lines. They represent the limits for the questionable and unsatisfactory results.

E_n - number

The normalised deviations [17] (E_n) were calculated according to:

$$E_n = \frac{x_i - X}{\sqrt{U_{x_i}^2 + U_X^2}} \tag{2}$$

where 'X' is the assigned/reference value with an expanded uncertainty 'U_X' and 'x_i' is the participant's average value with an expanded uncertainty 'U_{Xi}'. Satisfactory results are the ones for which $|E_n| \le 1$.

In Figure 6 to Figure 10 the biases of each participant (xi-X) are plotted and error bars are used to denote the value of denominator of equation 2 $\left(\sqrt{U_{x_i}^2 + U_X^2}\right)$. These plots represent also the E_n-number evaluations where, considering the E_n criteria ($|E_n| \le 1$), all results with error bars touching or crossing x-axis are satisfactory. Reported standard uncertainties (Annex B) that are bigger than "standard deviation for proficiency assessments" (σ_p, Table 3) are considered not fit-for-purpose and are denoted with "*" in the x-axis of each figure.

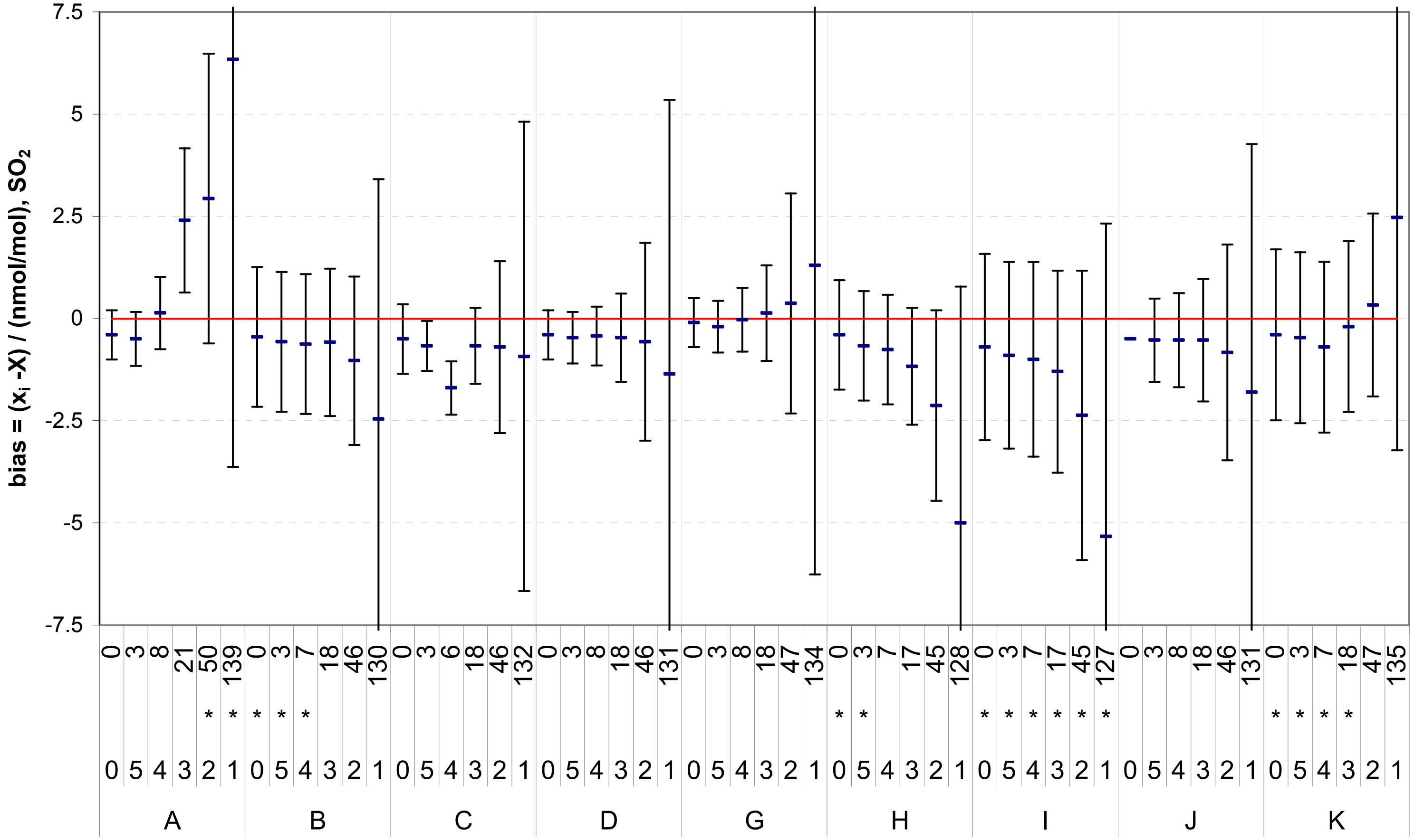

Figure 6: Bias of participant's SO_2 measurement results
together with the expanded uncertainty of bias presented with error bar are given for each tested concentration level. The results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger then σ_p.

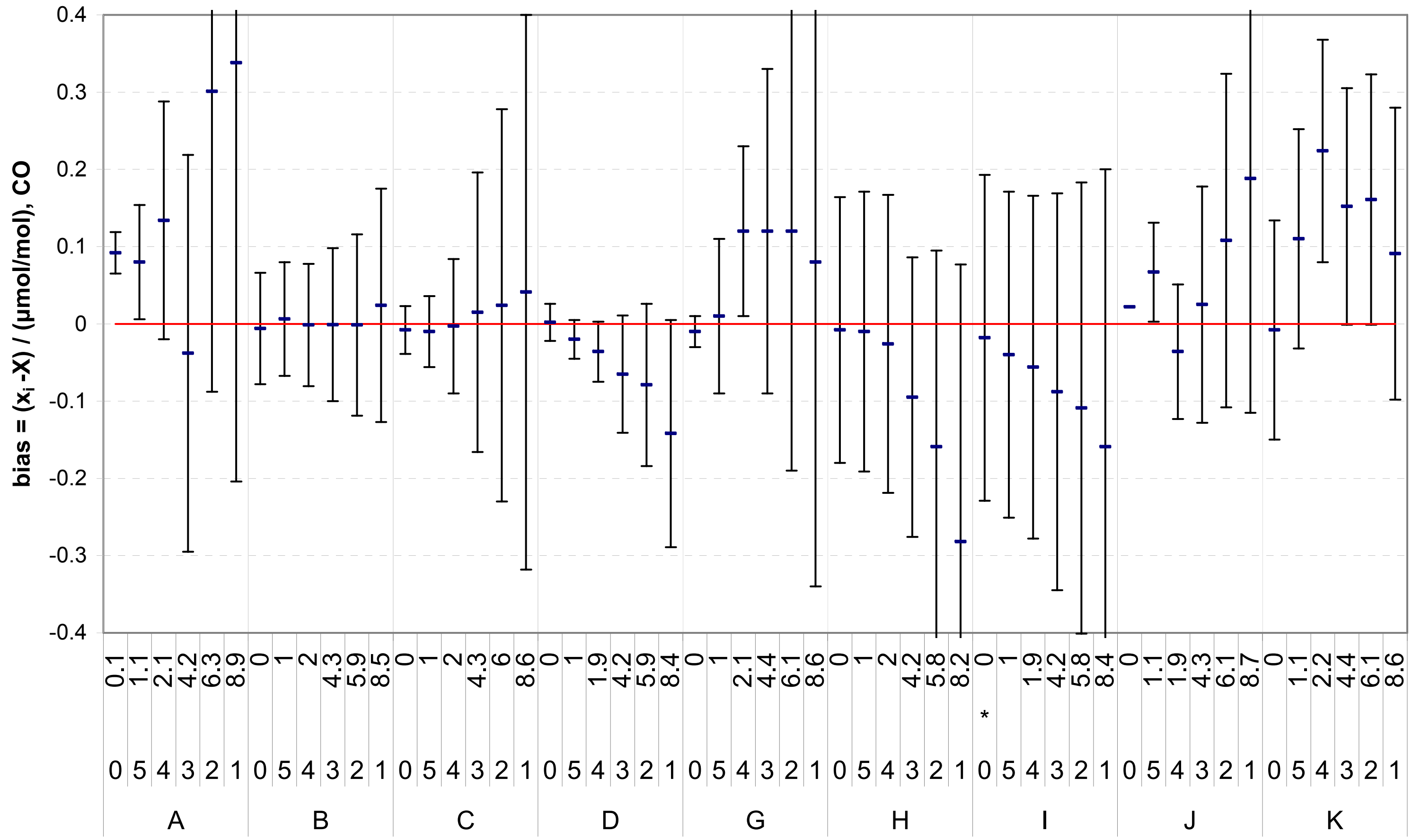

Figure 7: Bias of participant's CO measurement results
together with the expanded uncertainty of bias presented with error bar are given for each tested concentration level. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (µmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger then σ_p.

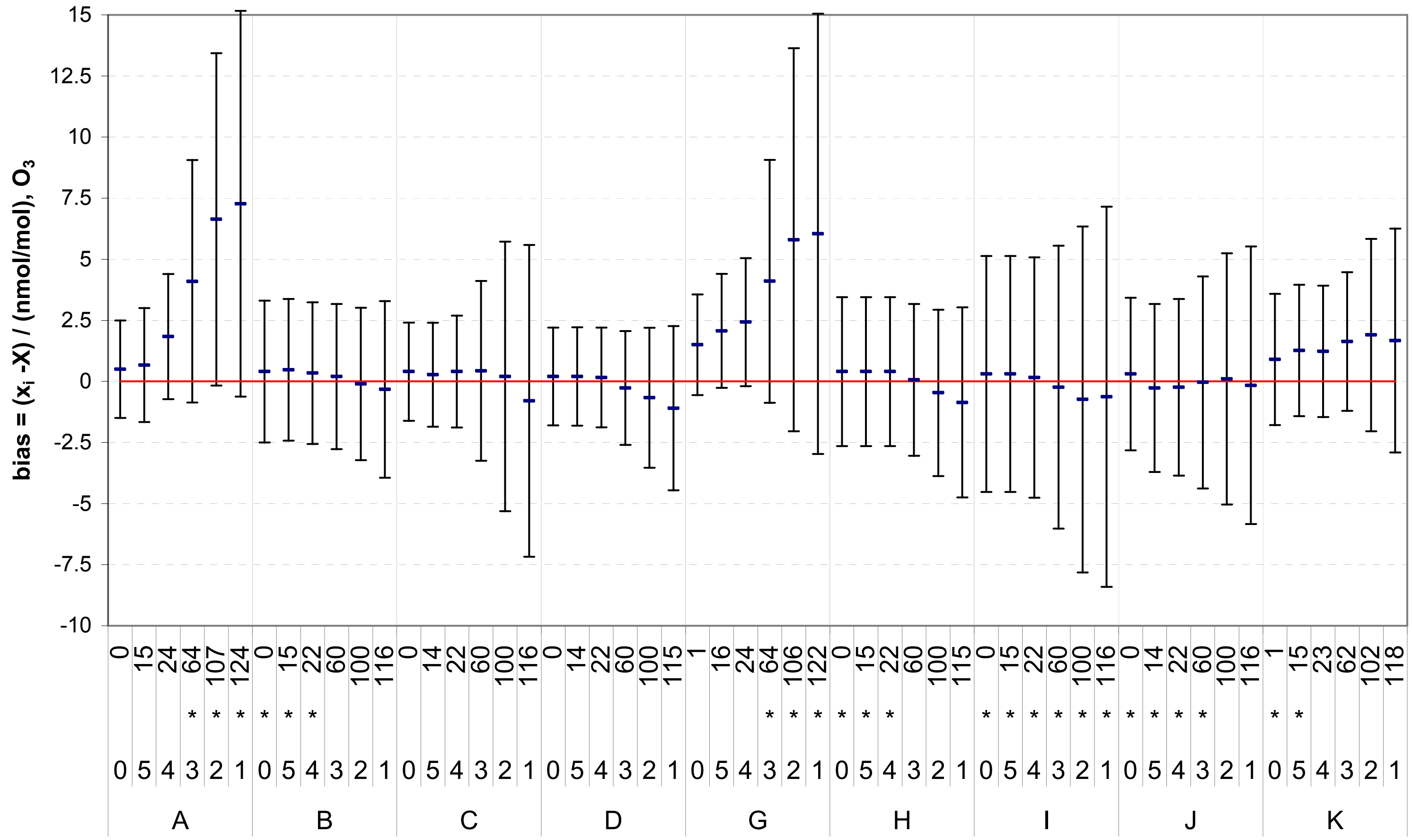

Figure 8: Bias of participant's O_3 measurement results
together with the expanded uncertainty of bias presented with error bar are given for each tested concentration level. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger then σ_p.

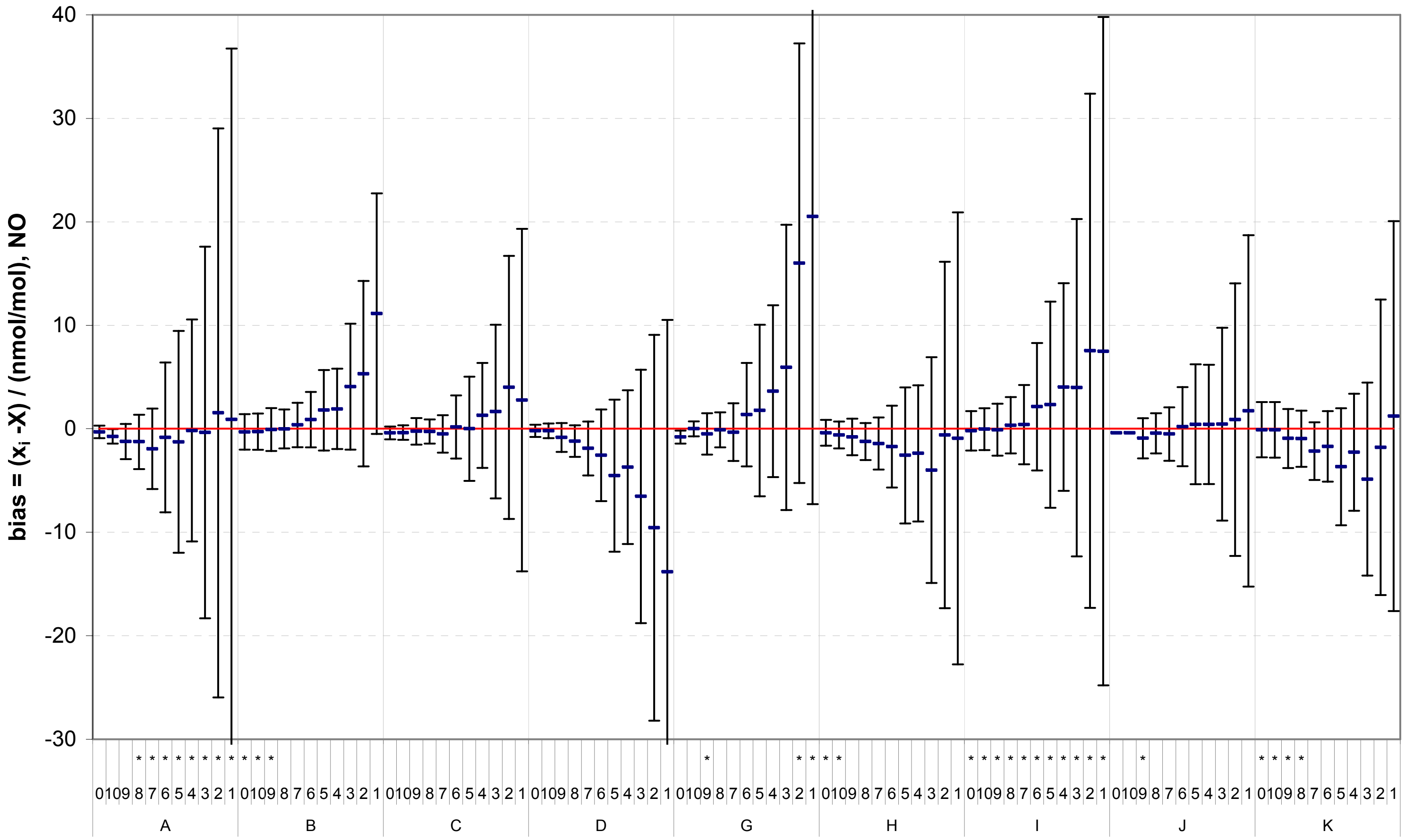

Figure 9: Bias of participant's NO measurement results
together with the expanded uncertainty of bias presented with error bar are given for each tested concentration level. Results with error bars touching or crossing the x-axis are satisfactory. Evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 nmol/mol), 10 (2 nmol/mol), 9 (16 nmol/mol), 8 (30 nmol/mol), 7 (50 nmol/mol) , 6 (90 nmol/mol) , 5 (150 nmol/mol) , 4 (150 nmol/mol) , 3 (250 nmol/mol) , 2 (380 nmol/mol), 1 (500 nmol/mol)). The '*' mark indicates reported standard uncertainties bigger then σ_p.

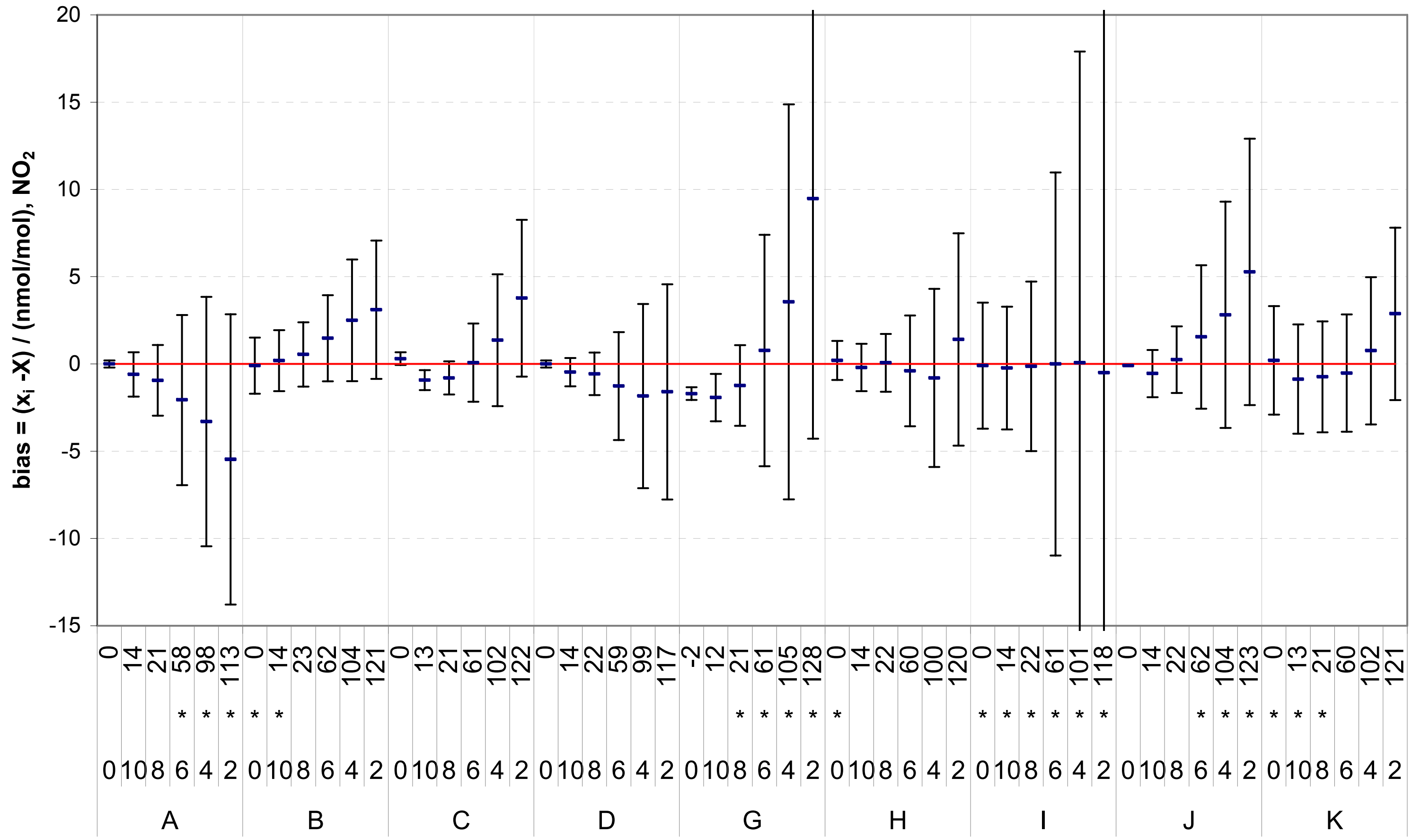

Figure 10: Bias of participant's NO_2 measurement results together with the expanded uncertainty of bias presented with error bar are given for tested concentration level with NO_2 run numbers 0, 2, 4, 6, 8 and 10 (see Table 2). Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger then σ_p.

6. Performance characteristics of individual laboratories

Individual participants' biases were evaluated and are presented in chapter 5 (Figure 6-Figure 10). Since the results of NO_2 runs 1,3,5,7 and 9 were not treated in the proficiency evaluation the biases of these runes are presented in Figure 11.

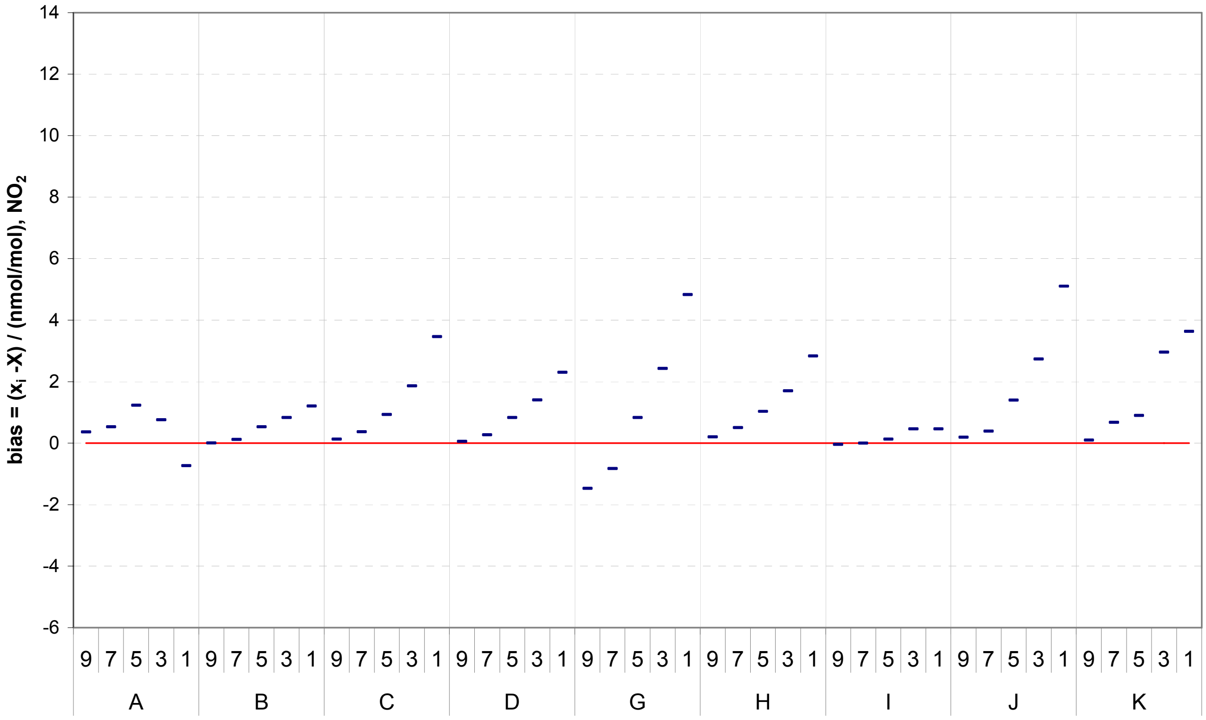

Figure 11: Bias of participant's NO_2 measurements for run numbers 1, 3, 5, 7 and 9
At these test gas mixtures the concentration levels of NO_2 were zero and the concentration levels of NO were not zero (see Table 2). In that perspective the figure shows the effect of NO concentration on NO_2 measurements.

The efficiency of NO_2-to-NO converters of NO_X analyzers

Since NO and NO_2 test gases were produced by gas phase titration it is possible to evaluate the efficiency of NO_2-to-NO converter of each participant's NO_X analyser. The evaluation takes each participants NO and NO_2 measurements before and after oxidation by O_3. The converter efficiency (α) is calculated using equation 3 [8]:

$$\alpha = \frac{[NO2]_i - [NO2]_{i-1}}{[NO]_{i-1} - [NO]_i} \cdot 100\% \qquad (3)$$

The O_3 measurements of each participant can also be compared to NO_2 measurements by calculating Δ using equation 4:

$$\Delta = [O3]_{i+1} - \left([NO2]_i - [NO2]_{i-1}\right) \qquad (4)$$

Ideal values for α and Δ are 100% and 0 nmol/mol respectively.

The first GPT test (at 120 ppb of NO_2) was jeopardised and discarded, because of the insufficient reproducibility of NO_X generation. The evaluation of equation 4 can not be made for the fifth GPT test (at 14 ppb of NO_2), because O_3 was not completely reduced due to insufficient excess of NO. The remaining evaluations of equations 3 and 4 for each participant at different concentration levels are given in Table 4.

Table 4: The efficiency of NO_2-to-NO converters.

IE code	NO_2 nmol/mol	α %	Δ (nmol/mol) nmol/mol
A	14	97.5	
A	22	96.6	2.9
A	60	95.5	6.5
A	100	96.9	10.0
B	14	100.8	
B	22	100.5	-0.5
B	60	100.3	-1.6
B	100	100.3	-2.5
C	14	92.4	
C	22	96.1	1.2
C	60	99.1	0.4
C	100	99.9	0.0
D	14	101.8	
D	22	99.7	0.6
D	60	100.1	1.0
D	100	100.4	1.8
E	14	100.9	
E	22	100.3	-0.4
E	60	100.3	-0.9
E	100	100.8	-0.7

IE code	NO_2 nmol/mol	α %	Δ (nmol/mol) nmol/mol
G	14	101.3	
G	22	99.5	2.4
G	60	99.5	3.3
G	100	99.6	3.9
H	14	99.5	
H	22	99.2	0.4
H	60	99.3	0.6
H	100	99.9	1.3
I	14	100.0	
I	22	99.4	-0.1
I	60	99.7	-1.0
I	100	100.4	-1.1
J	14	99.2	
J	22	100.0	-0.5
J	60	100.1	-1.1
J	100	100.8	-0.7
K	14	100.0	
K	22	99.3	2.2
K	60	101.2	2.2
K	100	101.2	3.4

The uncertainty of converter efficiency evaluation at higher NO_2 concentration is smaller then at lower NO_2 concentration. For the general feeling, the average standard uncertainty of the converter efficiency is calculated, by taking standard deviations of repeatable measurements of quantities in equation 3, and is evaluated to approximately 1%, at 100 nmol/mol of NO_2, and 3%, at 14 nmol/mol of NO_2.

7. Discussion

For a general assessment of the quality of each result a decision diagram was developed (Figure 12) that categorises results in seven categories (a1 to a7). The general comments for each category are:

- a1: measurement result is completely satisfactory
- a2: measurement result is satisfactory (z'-score satisfactory and En-number ok) but the reported uncertainty is too high
- a3: measured value is satisfactory (z'-score satisfactory) but the reported uncertainty is underestimated (En-number not ok)
- a4: measurement result is questionable (z'-score questionable) but due to a high reported uncertainty can be considered valid (En-number ok)
- a5: measurement result is questionable (z'-score questionable and En-number not ok)
- a6: measurement result is unsatisfactory (z'-score unsatisfactory) but due to a high reported uncertainty can be considered valid (En-number ok)
- a7: measurement result is unsatisfactory (z'-score unsatisfactory and En-number not ok)

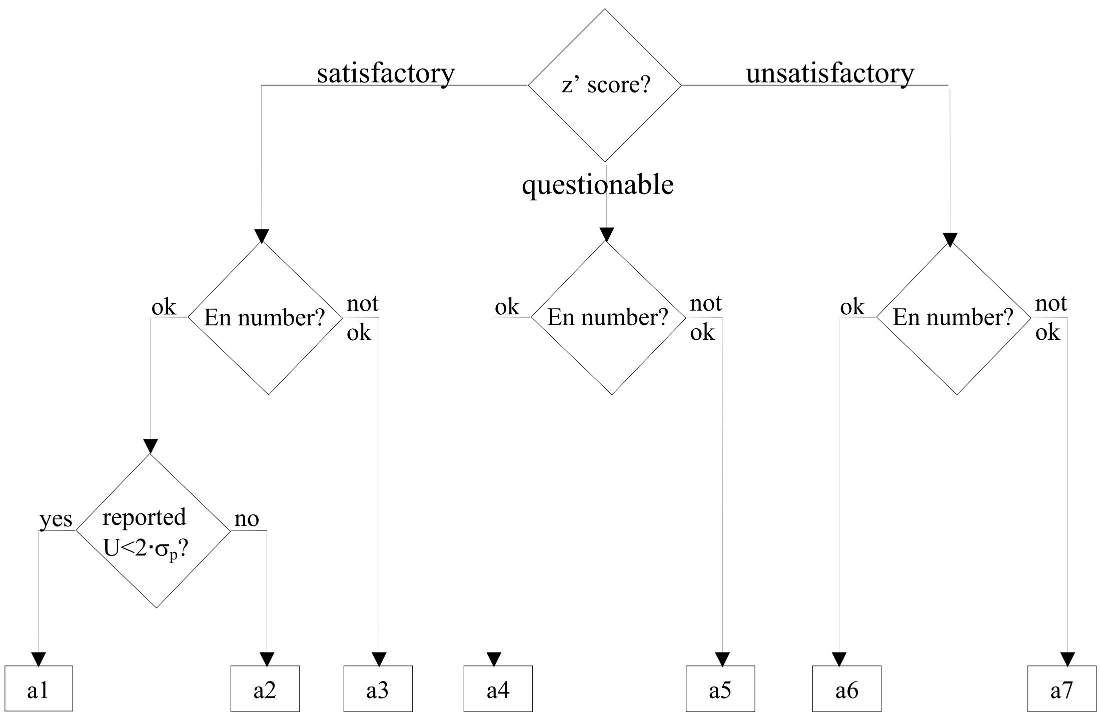

Figure 12: The decision diagram for general assessment of proficiency results.

The results of the IE were assigned to categories according to the diagram given in Figure 12 and are presented in Table 5. For clarity reasons, notation 'a1' is not inserted in Table 5 and all empty spaces represent 'a1' results.

Table 5: The general assessment of proficiency results.
Empty spaces represent 'a1' results.

	run number	conc. level	IE code								
			A	B	C	D	G	H	I	J	K
SO_2 (nmol/mol)	0	1		a2				a2	a2	a3	a2
	5	4		a2	a3			a2	a2		a2
	4	8		a2	a5				a2		a2
	3	18	a5						a2		a2
	2	47	a2						a2		
	1	133	a2						a2		
CO (µmol/mol)	0	0	a3						a2	a3	
	5	1	a3							a3	
	4	2					a3				a3
	3	4.3									
	2	5.9									
	1	8.5									
O_3 (nmol/mol)	0	0		a2				a2	a2	a2	a2
	5	14		a2				a2	a2	a2	a2
	4	22		a2				a2	a2	a2	
	3	60	a2				a2		a2	a2	
	2	100	a4				a2		a2		
	1	116	a4				a2		a2		
NO (nmol/mol)	0	0		a2			a3	a2	a2	a3	a2
	10	2	a3	a2				a2	a2	a3	a2
	9	16		a2			a2		a2	a2	a2
	8	29	a2						a2		a2
	7	51	a2						a2		
	6	90	a2						a2		
	5	151	a2						a2		
	4	151	a2						a2		
	3	251	a2						a2		
	2	383	a2				a2		a2		
	1	502	a2				a2		a2		
NO_2 (nmol/mol)	0	0		a2			a7	a2	a2	a3	a2
	10	14		a2	a3		a5		a2		a2
	8	22					a2		a2		a2
	6	61	a2				a2		a2	a2	
	4	101	a2				a2		a2	a2	
	2	118	a2				a4		a2	a2	

.

8. Conclusions

The proficiency evaluation scheme has provided an assessment of the participants measured values and their evaluated uncertainties. In terms of the criteria imposed by the European Commission (σp) 60% of the results reported by AQUILA laboratories fall into 'a1' category and are good both in terms of measured values and evaluated uncertainties. In residual 37% of the results have good measured values but the evaluated uncertainties were either too high, category 'a2' (33%), or too small, category 'a3' (4%). The relative high number of 'a2'cases, where participant's evaluated uncertainty is higher then the common IE criterion, needs further investigation. The common IE criterion is confirmed to be realistic by comparison to reproducibility standard deviation obtained at this IE (Annex C) and is derived from the European standards' uncertainty requirements, which are explicit at high concentrations. Since the uncertainty requirements at zero concentration are not quantitatively stated in the European standards, the IE criteria at zero concentration had to be set within AQUILA. The initially proposed values were in use for IEs since June 2007 to October 2008 but at the November 2008 AQUILA meeting the IE criteria at zero concentration were enlarged and approved. The final values were also communicated to relevant CEN working group for potential future amendments of European standards. With that in mind especially 'a2' results at high concentration levels should be further investigated by the NRLs.

Two NRLs (participants A and G) have overall unsatisfactory results of the z'-score evaluation (one unsatisfactory, categories 'a6' or 'a7', or two questionable, categories 'a4' or 'a5', result per parameter) which in the view of AQUILA requires participation to the next IE in order to demonstrate remediation measures.

The comparability of results among AQUILA participants is best for O_3 and worst for NO_2 measurement method. The relative reproducibility limits, at the highest studied concentration levels, are 7.1% for SO_2, 7.3% for CO, 3.0% for O_3 and 6.1% for NO which are all below the objective derived from criteria imposed by the European Commission (σp). This is not the case for NO_2 where the relative reproducibility limit is 11.8% and the objective is 8.8% and is therefore generally considered as unsatisfactory. The NO_2 reproducibility limit was evaluated for the test mixture where beside NO_2 also NO was present. To achieve objective in such conditions, investigations should focus on converter efficiency and traceability of gas standards. For the latter case the uncertainties of both NO and NO_2 amount in the gas standard should be reduced.

9. References

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Annex A. Assigned values

The assigned values of tested concentration levels were derived from ERLAPs measurements which are calibrated against the certified reference values of CRMs and are traceable to international standards. In this perspective the assigned values are reference values as defined in the ISO 13528 [17].

ERLAPs SO_2, CO and NO analysers were calibrated according to the methodology described in the ISO 6143 [10]. A different number (4 for SO_2, 7 for CO and 5 for NO) of reference gas mixtures were produced from the primary reference materials (produced and certified by NMi Van Swinden Laboratorium) by dynamic dilution method using mass flow controllers [12]. All flows were measured with a certified volumeter. For the evaluation of concentration values and the uncertainties of reference gas mixtures and the evaluation of calibrations two computer applications were used, the "GUM WORKBENCH" [27] and "B-least" [28] respectively. For extending calibration from the NO to NO_2 channel of NO_X analyser, two additional calibrations/tests were preformed. First, the NO_2-converter was "bridged" (NO_2-converter was disconnected and in its place a Teflon tube was inserted) and at different NO concentration levels the NO_X channel was calibrated against the NO channel. Secondly, the GPT test was performed to establish the efficiency of NO_2-converter. For IEs test gas concentration levels ERLAPs NO_2 measurements were evaluated by the following equation:

$$[NO_2] = \frac{k \cdot (a \cdot [NO_X] + b - [NO])}{\alpha} \qquad (5)$$

Where 'a' and 'b' denote parameters from the linear calibration of NO_X channel against NO channel, 'k' denotes the slope of linear calibration of NO channel against NO reference gas mixtures and 'α' denotes the efficiency of NO_2-converter. In the evaluation of NO_2 uncertainty all these quantities have insignificant correlation. For O_3 measurements, the primary standard was used.

ERLAP's measurement results were validated by comparison to the group statistics (x* and s*) for every parameter and concentration level of the IE. These statistics are calculated from participating NRLs, applying the robust method described in the Annex C of ISO 13528 [17]. The validation is taking in account ERLAP's value (X) and its standard uncertainty ($u_{X'}$) as given in expression 6 [17]:

$$\frac{|x^* - X|}{\sqrt{\frac{(1{,}25 \cdot s^*)^2}{p} + u_{X'}^2}} < 2 \qquad (6)$$

Where 'x*' and 's*' represent robust average and robust standard deviation respectively and 'p' is the number of NRLs.

In Table 6 all inputs for expression 6 are given and all ERLAP's measurement results are confirmed to be valid.

Table 6: The validation of assigned values (X)
by comparison to the robust averages (x*) with taking into the account the standard uncertainties of assigned values (uX'), and robust standard deviations (s*) as denoted by expression 6.

run	unit	X	uX	x*	s*	val.	run	unit	X	uX	x*	s*	val.
CO _0	µmol/mol	0.008	0.012	0.0033	0.0065	OK	NO _0	nmol/mol	0.4	0.3	0.11	0.16	OK
CO _1	µmol/mol	8.5193	0.057	8.538	0.173	OK	NO _1	nmol/mol	501.8	3.4	503.83	3.43	OK
CO _2	µmol/mol	5.9487	0.041	5.9795	0.1437	OK	NO _2	nmol/mol	383.13	2.6	385.07	4.71	OK
CO _3	µmol/mol	4.2753	0.03	4.2731	0.0839	OK	NO _3	nmol/mol	251.3	1.8	251.33	4.67	OK
CO _4	µmol/mol	1.9763	0.017	1.9823	0.0564	OK	NO _4	nmol/mol	151.07	1.1	151.35	2.9	OK
CO _5	µmol/mol	0.99	0.011	0.997	0.0323	OK	NO _5	nmol/mol	150.9	1.1	150.39	2.58	OK
O3 _0	nmol/mol	-0.3	1	0.09	0.18	OK	NO _6	nmol/mol	90.33	0.7	90.14	1.65	OK
O3 _1	nmol/mol	116.33	1.4	116.26	0.96	OK	NO _7	nmol/mol	50.93	0.5	50.13	1.11	OK
O3 _2	nmol/mol	100.27	1.2	100.53	0.98	OK	NO _8	nmol/mol	28.83	0.4	28.32	0.68	OK
O3 _3	nmol/mol	59.87	1.1	60.15	0.52	OK	NO _9	nmol/mol	15.77	0.6	15.21	0.5	OK
O3 _4	nmol/mol	21.77	1	22.2	0.51	OK	NO _10	nmol/mol	1.97	0.4	1.71	0.27	OK
O3 _5	nmol/mol	14.2	1	14.59	0.39	OK	NO2 _0	nmol/mol	0.1	0.1	0.11	0.17	OK
SO2 _0	nmol/mol	0.5	0.3	0.09	0.12	OK	NO2 _1	nmol/mol	-0.43	0.9	1.88	2.29	OK
SO2 _1	nmol/mol	132.53	1.2	131.52	3.21	OK	NO2 _2	nmol/mol	118.2	1.3	120.05	3.68	OK
SO2 _2	nmol/mol	47	0.5	46.42	1.25	OK	NO2 _3	nmol/mol	0.07	0.9	1.58	1.13	OK
SO2 _3	nmol/mol	18.3	0.3	17.86	0.61	OK	NO2 _4	nmol/mol	101.07	1.1	101.61	2.38	OK
SO2 _4	nmol/mol	8.03	0.3	7.51	0.5	OK	NO2 _5	nmol/mol	-0.23	0.5	0.6	0.41	OK
SO2 _5	nmol/mol	3.6	0.3	3.08	0.18	OK	NO2 _6	nmol/mol	60.5	0.7	60.51	1.13	OK
							NO2 _7	nmol/mol	0	0.3	0.27	0.3	OK
							NO2 _8	nmol/mol	22.17	0.3	21.81	0.66	OK
							NO2 _9	nmol/mol	0.17	0.6	0.25	0.14	OK
							NO2 _10	nmol/mol	14.1	0.2	13.61	0.51	OK

Prior to the IE, the homogeneity and stability of gas mixture in the distribution line of ERLAP laboratory has been investigated. The effect of unstable concentration of test gas on repeatability evaluations is further diminished by taking and reporting half-hour averages. The homogeneity of test gas concentrations in the distribution line was evaluated from previous experiences and from paired O_3 measurements during the IE. The upper and lower limits of bias due to homogeneity was evaluated to be smaller than 1% which constitutes the expanded standard uncertainty of 1,2% of tested concentration level. The standard uncertainties of assigned/reference values (u_X) were calculated with equation 7 and used in the proficiency evaluations of chapter 5.

$$u_X^2 = u_{X'}^2 + \left(X \cdot u_{\mathrm{hom}ogin ety}\right)^2 \qquad (7)$$

Annex B. Results of the IE

The reported values, presented also in graphs, are given in this annex. The participants were asked to report results (x_{ij}, $u(x_i)$ and $U(x_i)$) expressed in mol/mol units. For all the runs except concentration levels 0, also each participant's average (x_i) and standard deviation (s_i) are presented. As a group evaluation robust average (x*) and robust standard deviation (s*) were calculated (applying the procedure described in Annex C of ISO 13528) for each run, and are presented in the following tables. The assigned value is indicated on the graphs with the red line and the individual laboratories expanded uncertainties ($U(x_i)$) are indicated with error bars.

Reported values for SO_2

Table 7: Reported values for SO_2 concentration level 0.

parameter: SO2 all units are nmol/mol
level: 0 x*: 0.1 s*: 0.1

	A	B	C	D	E	G	H	I	J	K
xi,1	0.10	0.05	0.0	0.1	0.5	0.4	0.1	-0.2	0.0	0.1
u(xi)	0.006	0.82	0.30	0.0	0.3	0.0	0.6	1.1		1.0
U(xi)	0.012	1.6	0.60	0.0	0.6	0.0	1.2	2.2		2.0

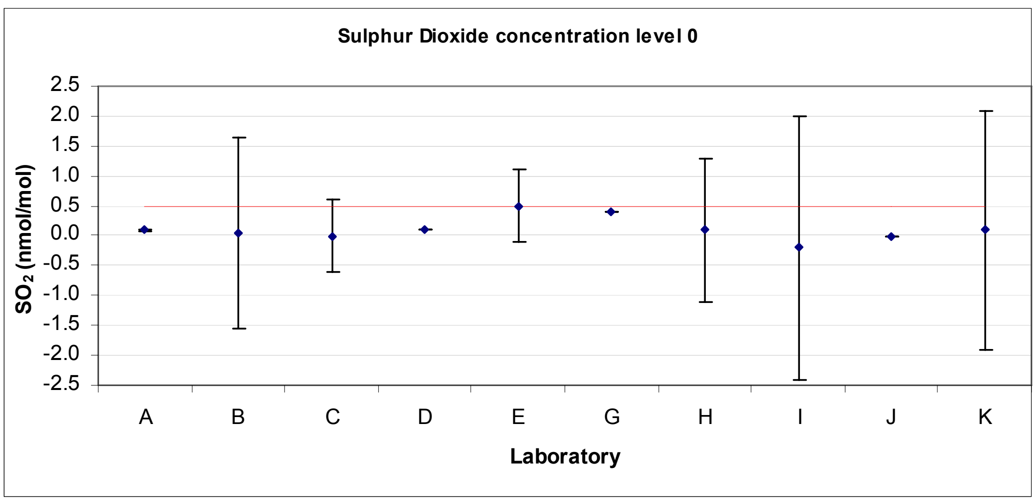

Figure 13: Reported values for SO_2 concentration level 0.

Table 8: Reported values for SO_2 concentration level 1.

parameter: SO2 level: 1	all units are nmol/mol x*: 131.52 s*: 3.21									
	A	B	C	D	E	G	H	I	J	K
xi,1	138.80	129.8	131.3	131.0	132.4	133.8	127.2	127.1	130.7	134.9
xi,2	138.90	130.1	131.6	131.2	132.6	133.8	127.7	127.2	130.7	135.1
xi,3	138.90	130.3	131.9	131.3	132.6	133.9	127.7	127.3	130.8	135.0
xi	138.867	130.07	131.60	131.17	132.53	133.83	127.53	127.20	130.73	135.00
si	0.058	0.25	0.30	0.15	0.12	0.06	0.29	0.10	0.06	0.10
u(xi)	4.80	2.72	2.63	3.1	0.9	3.6	2.6	3.6	2.81	2.6
U(xi)	9.70	5.4	5.26	6.3	1.8	7.2	5.3	7.3	5.62	5.2

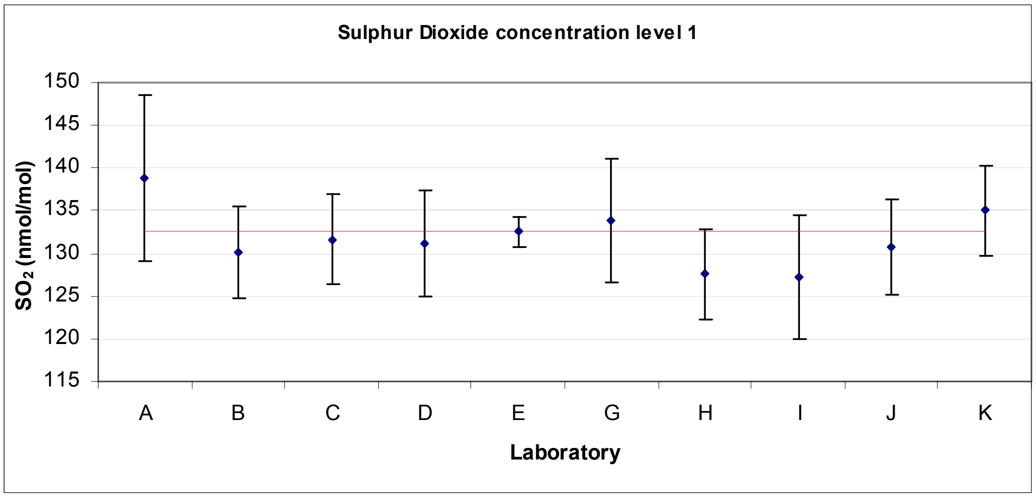

Figure 14: Reported values for SO_2 concentration level 1.

Table 9: Reported values for SO_2 concentration level 2.

parameter: SO2 level: 2	all units are nmol/mol x*: 46.42 s*: 1.25									
	A	B	C	D	E	G	H	I	J	K
xi,1	49.80	46.07	46.2	46.5	47.0	47.4	45.0	44.6	46.3	47.4
xi,2	50.00	45.97	46.3	46.4	47.0	47.3	44.8	44.6	46.1	47.4
xi,3	50.00	45.86	46.4	46.4	47.0	47.4	44.8	44.7	46.1	47.2
xi	49.933	45.967	46.30	46.43	47.00	47.37	44.87	44.63	46.17	47.33
si	0.115	0.105	0.10	0.06	0.00	0.06	0.12	0.06	0.12	0.12
u(xi)	1.80	0.90	0.93	1.1	0.4	1.3	1.0	1.7	1.22	1.0
U(xi)	3.40	1.8	1.85	2.2	0.9	2.5	2.1	3.4	2.44	2.0

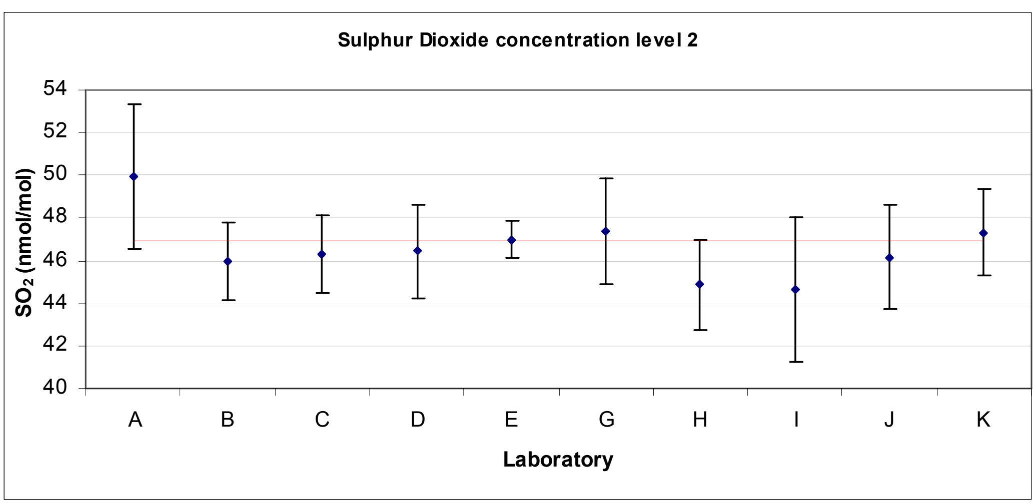

Figure 15: Reported values for SO_2 concentration level 2.

Table 10: Reported values for SO_2 concentration level 3.

parameter: SO2, level: 3 — all units are nmol/mol — x*: 17.86 s*: 0.61

	A	B	C	D	E	G	H	I	J	K
xi,1	20.10	17.69	17.6	17.8	18.3	18.4	17.2	17.0	17.8	18.1
xi,2	21.00	17.69	17.7	17.8	18.3	18.5	17.1	17.0	17.8	18.1
xi,3	21.00	17.77	17.6	17.9	18.3	18.4	17.1	17.0	17.7	18.1
xi	20.700	17.717	17.63	17.83	18.30	18.43	17.13	17.00	17.77	18.10
si	0.520	0.046	0.06	0.06	0.00	0.06	0.06	0.00	0.06	0.00
u(xi)	0.83	0.83	0.35	0.4	0.3	0.5	0.6	1.2	0.69	1.0
U(xi)	1.66	1.7	0.71	0.9	0.6	1.0	1.3	2.4	1.38	2.0

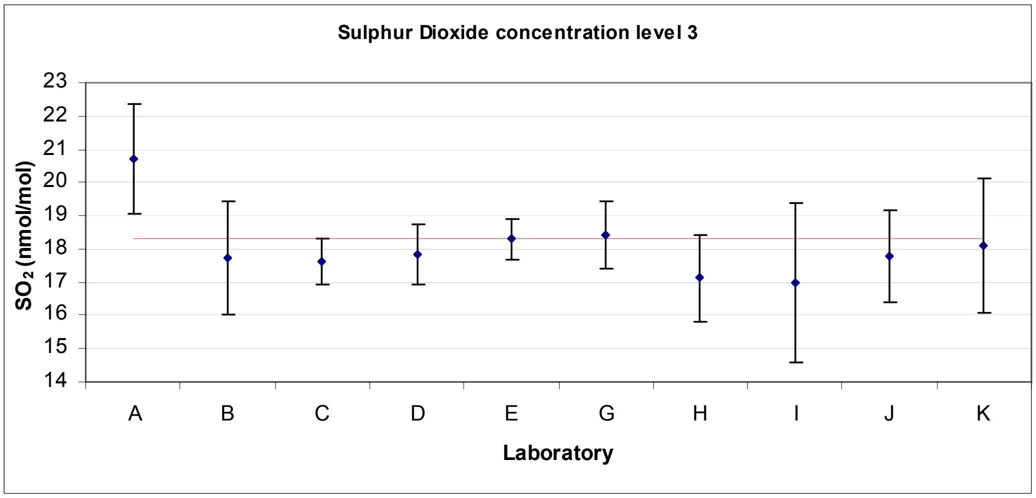

Figure 16: Reported values for SO_2 concentration level 3.

Table 11: Reported values for SO_2 concentration level 4.

parameter: SO2, level: 4 — all units are nmol/mol — x*: 7.51 s*: 0.50

	A	B	C	D	E	G	H	I	J	K
xi,1	8.10	7.39	6.4	7.6	8.1	8.0	7.3	7.0	7.5	7.3
xi,2	8.20	7.41	6.3	7.6	8.0	8.0	7.3	7.0	7.5	7.3
xi,3	8.20	7.41	6.3	7.6	8.0	8.0	7.2	7.1	7.5	7.4
xi	8.167	7.403	6.33	7.60	8.03	8.00	7.27	7.03	7.50	7.33
si	0.058	0.012	0.06	0.00	0.06	0.00	0.06	0.06	0.00	0.06
u(xi)	0.32	0.82	0.13	0.2	0.3	0.2	0.6	1.1	0.49	1.0
U(xi)	0.65	1.6	0.25	0.4	0.6	0.5	1.2	2.3	0.98	2.0

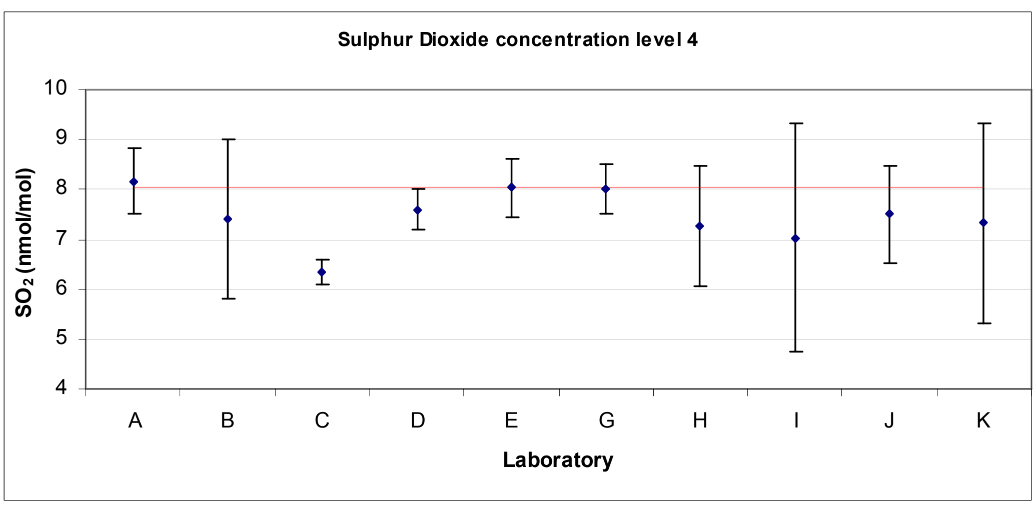

Figure 17: Reported values for SO_2 concentration level 4.

Table 12: Reported values for SO_2 concentration level 5.

parameter: SO2 — all units are nmol/mol
level: 5 — x*: 3.08 — s*: 0.18

	A	B	C	D	E	G	H	I	J	K
xi,1	3.10	3.06	3.0	3.2	3.6	3.4	2.9	2.7	3.1	3.4
xi,2	3.10	3.03	2.9	3.1	3.6	3.4	2.9	2.7	3.1	3.0
xi,3	3.10	3.00	2.9	3.1	3.6	3.4	3.0	2.7	3.0	3.0
xi	3.100	3.030	2.93	3.13	3.60	3.40	2.93	2.70	3.07	3.13
si	0.000	0.030	0.06	0.06	0.00	0.00	0.06	0.00	0.06	0.23
u(xi)	0.14	0.82	0.06	0.1	0.3	0.1	0.6	1.1	0.41	1.0
U(xi)	0.28	1.6	0.12	0.2	0.6	0.2	1.2	2.2	0.82	2.0

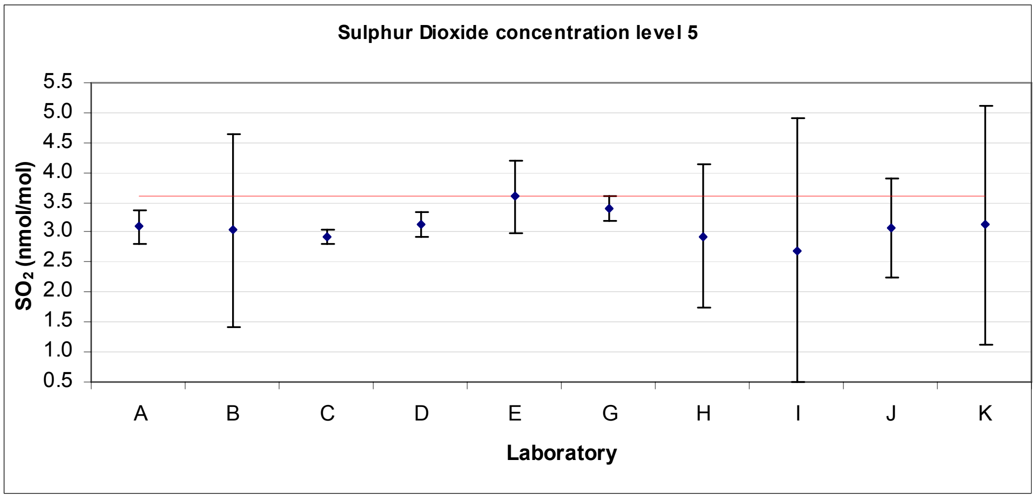

Figure 18: Reported values for SO_2 concentration level 5.

Reported values for CO

Table 13: Reported values for CO concentration level 0.

parameter: CO — all units are µmol/mol
level: 0 — x*: 0.00 — s*: 0.01

	A	B	C	D	E	G	H	I	J	K
xi,1	0.100	0.002	0.00	0.01	0.008	0.0	0.00	-0.01	0.03	0.00
u(xi)	0.006	0.034	0.01	0.000	0.012	0.0	0.08	0.10		0.07
U(xi)	0.012	0.068	0.02	0.000	0.024	0.0	0.17	0.21		0.14

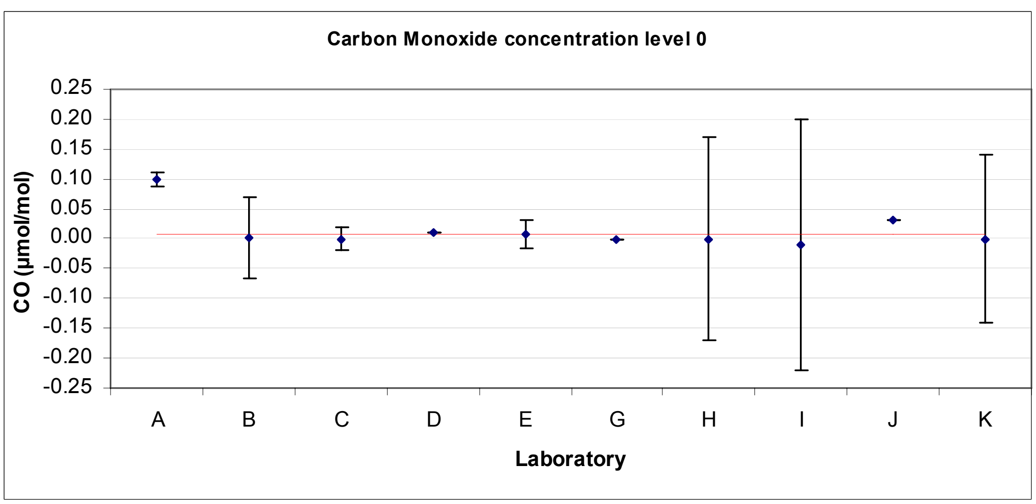

Figure 19: Reported values for CO concentration level 0.

Table 14: Reported values for CO concentration level 1.

parameter: CO   all units are µmol/mol
level: 1   x*: 8.54   s*: 0.17

	A	B	C	D	E	G	H	I	J	K
xi,1	8.85	8.542	8.56	8.37	8.519	8.6	8.24	8.36	8.71	8.61
xi,2	8.86	8.541	8.57	8.38	8.521	8.6	8.23	8.36	8.71	8.61
xi,3	8.86	8.547	8.55	8.38	8.518	8.6	8.24	8.36	8.70	8.61
xi	8.857	8.5433	8.560	8.377	8.5193	8.60	8.237	8.360	8.707	8.610
si	0.006	0.0032	0.010	0.006	0.0015	0.00	0.006	0.000	0.006	0.000
u(xi)	0.27	0.049	0.17	0.050	0.030	0.2	0.17	0.17	0.14	0.07
U(xi)	0.53	0.098	0.34	0.092	0.060	0.4	0.34	0.34	0.28	0.15

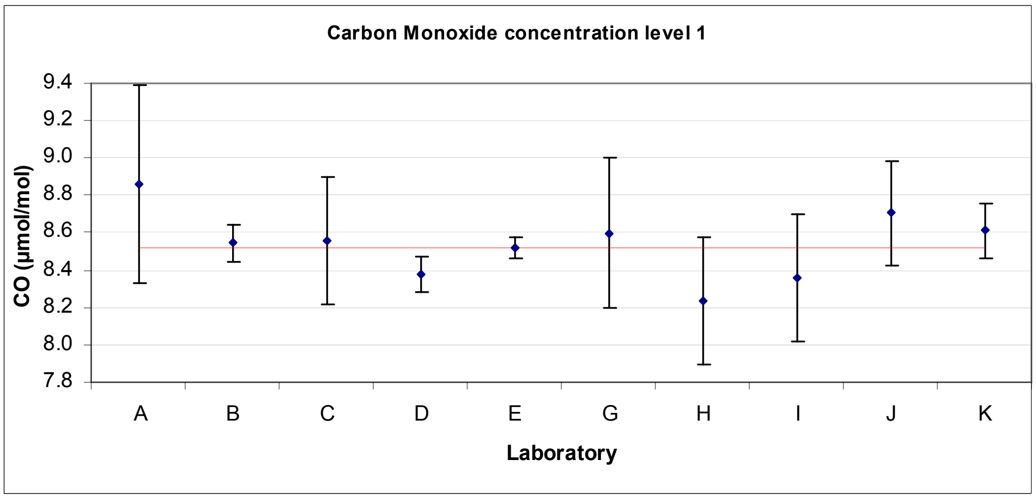

Figure 20: Reported values for CO concentration level 1.

Table 15: Reported values for CO concentration level 2.

parameter: CO   all units are µmol/mol
level: 2   x*: 5.98   s*: 0.14

	A	B	C	D	E	G	H	I	J	K
xi,1	6.25	5.944	5.98	5.87	5.949	6.1	5.79	5.84	6.07	6.11
xi,2	6.25	5.947	5.96	5.87	5.948	6.0	5.79	5.84	6.07	6.11
xi,3	6.25	5.951	5.98	5.87	5.949	6.1	5.79	5.84	6.03	6.11
xi	6.250	5.9473	5.973	5.870	5.9487	6.07	5.790	5.840	6.057	6.110
si	0.000	0.0035	0.012	0.000	0.0006	0.06	0.000	0.000	0.023	0.000
u(xi)	0.19	0.042	0.12	0.035	0.022	0.2	0.12	0.14	0.10	0.07
U(xi)	0.38	0.084	0.24	0.065	0.044	0.3	0.24	0.28	0.20	0.14

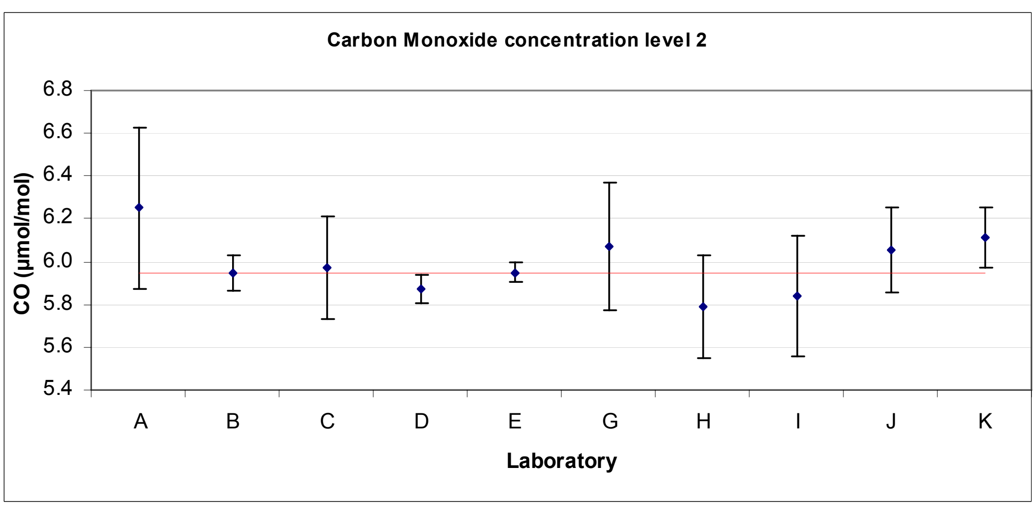

Figure 21: Reported values for CO concentration level 2.

Table 16: Reported values for CO concentration level 3.

parameter: CO level: 3	all units are µmol/mol x*: 4.27	s*: 0.08								
	A	B	C	D	E	G	H	I	J	K
xi,1	4.23	4.268	4.29	4.21	4.273	4.4	4.18	4.19	4.28	4.43
xi,2	4.24	4.275	4.29	4.21	4.276	4.4	4.18	4.19	4.31	4.43
xi,3	4.24	4.280	4.29	4.21	4.277	4.4	4.18	4.18	4.31	4.42
xi	4.237	4.2743	4.290	4.210	4.2753	4.40	4.180	4.187	4.300	4.427
si	0.006	0.0060	0.000	0.000	0.0021	0.00	0.000	0.006	0.017	0.006
u(xi)	0.13	0.039	0.09	0.025	0.018	0.1	0.08	0.12	0.07	0.07
U(xi)	0.25	0.078	0.17	0.046	0.036	0.2	0.17	0.25	0.14	0.14

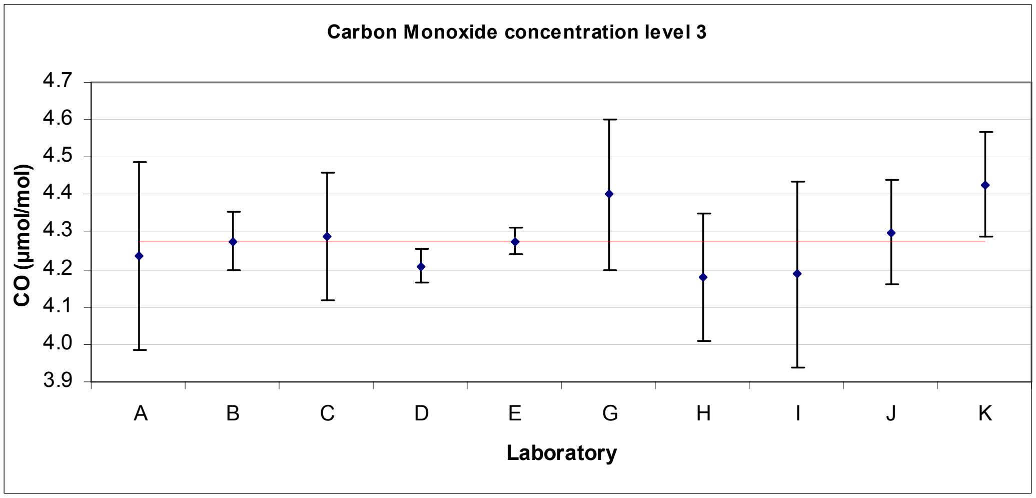

Figure 22: Reported values for CO concentration level 3.

Table 17: Reported values for CO concentration level 4.

parameter: CO level: 4	all units are µmol/mol x*: 1.98	s*: 0.06								
	A	B	C	D	E	G	H	I	J	K
xi,1	2.11	1.970	1.98	1.94	1.976	2.1	1.95	1.92	1.94	2.20
xi,2	2.11	1.976	1.97	1.94	1.977	2.1	1.95	1.92	1.94	2.20
xi,3	2.11	1.979	1.97	1.94	1.976	2.1	1.95	1.92	1.94	2.20
xi	2.110	1.9750	1.973	1.940	1.9763	2.10	1.950	1.920	1.940	2.200
si	0.000	0.0046	0.006	0.000	0.0006	0.00	0.000	0.000	0.000	0.000
u(xi)	0.08	0.036	0.04	0.012	0.012	0.1	0.09	0.11	0.04	0.07
U(xi)	0.15	0.072	0.08	0.021	0.024	0.1	0.19	0.22	0.08	0.14

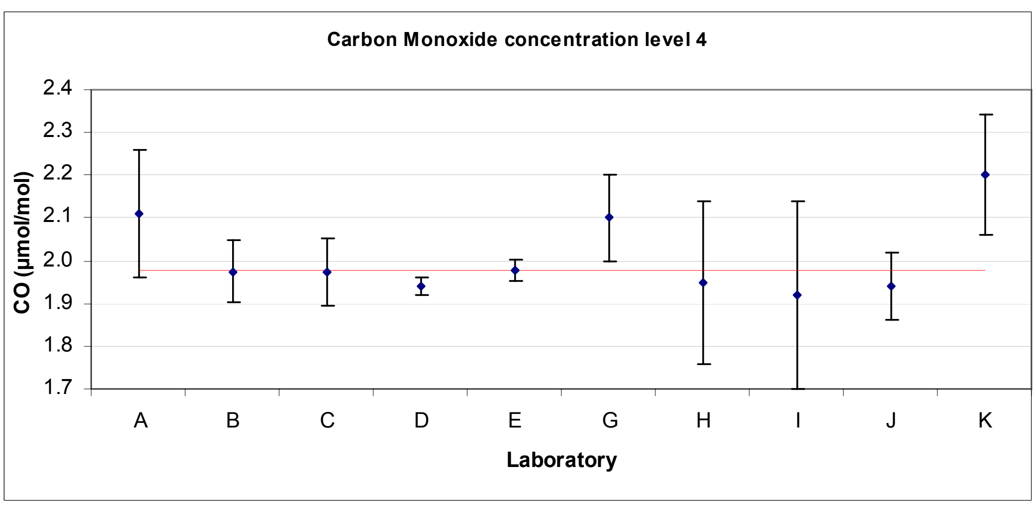

Figure 23: Reported values for CO concentration level 4.

Table 18: Reported values for CO concentration level 5.

parameter: CO — all units are µmol/mol
level: 5 — x*: 1.00 — s*: 0.03

	A	B	C	D	E	G	H	I	J	K
xi,1	1.07	0.995	0.98	0.97	0.991	1.0	0.98	0.95	1.06	1.10
xi,2	1.07	0.996	0.98	0.97	0.991	1.0	0.98	0.95	1.05	1.10
xi,3	1.07	0.998	0.98	0.97	0.988	1.0	0.98	0.95	1.06	1.10
xi	1.070	0.9963	0.980	0.970	0.9900	1.00	0.980	0.950	1.057	1.100
si	0.000	0.0015	0.000	0.000	0.0017	0.00	0.000	0.000	0.006	0.000
u(xi)	0.04	0.035	0.02	0.006	0.010	0.0	0.09	0.10	0.03	0.07
U(xi)	0.07	0.070	0.04	0.011	0.020	0.1	0.18	0.21	0.06	0.14

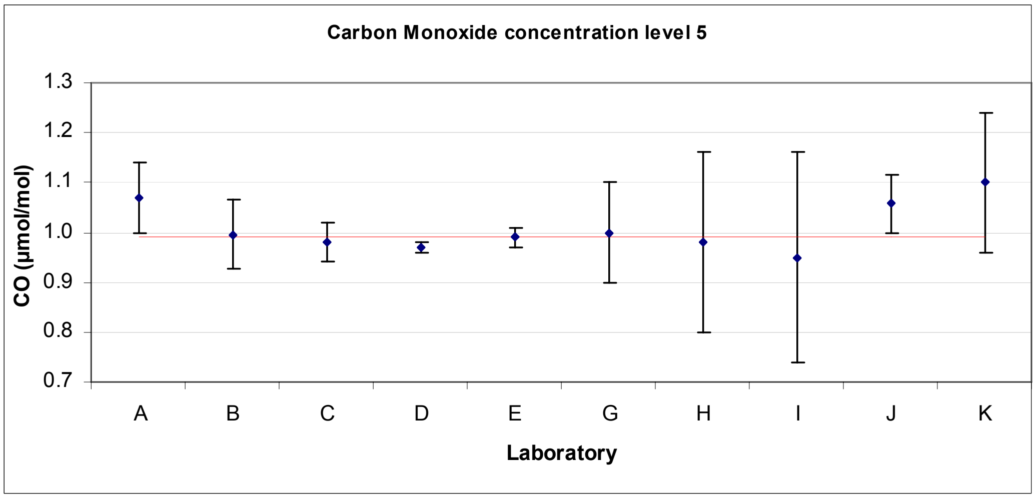

Figure 24: Reported values for CO concentration level 5.

Reported values for O3

Table 19: Reported values for O3 concentration level 0.

parameter: O3 — all units are nmol/mol
level: 0 — x*: 0.09 — s*: 0.18

	A	B	C	D	E	G	H	I	J	K
xi,1	0.200	0.1	0.1	-0.1	-0.3	1.2	0.1	0.0	0.0	0.6
u(xi)	0.006	1.04	0.09	0.0	1.0	0.2	1.1	2.2	1.2	0.9
U(xi)	0.012	2.1	0.18	0.0	2.0	0.5	2.3	4.4	2.4	1.8

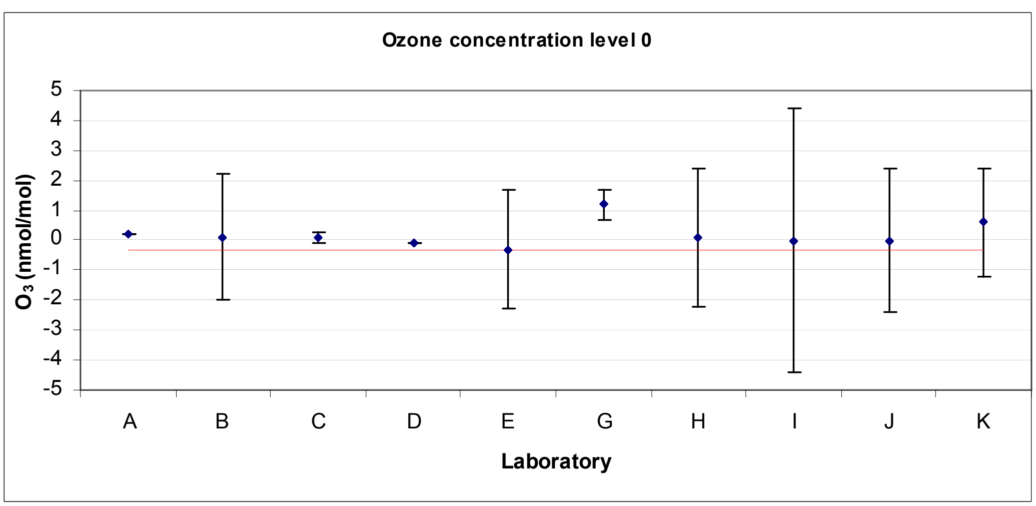

Figure 25: Reported values for O3 concentration level 0.

Table 20: Reported values for O3 concentration level 1.

parameter: O3	all units are nmol/mol									
level: 1	x*: 116.26		s*: 0.96							
	A	B	C	D	E	G	H	I	J	K
xi,1	122.90	115.6	114.7	114.8	116.0	121.8	115.1	115.0	115.6	117.5
xi,2	123.80	116.1	115.5	115.3	116.4	122.5	115.6	115.5	116.3	118.1
xi,3	124.10	116.3	116.4	115.6	116.6	122.8	115.7	116.6	116.6	118.4
xi	123.600	116.00	115.53	115.23	116.33	122.37	115.47	115.70	116.17	118.00
si	0.624	0.36	0.85	0.40	0.31	0.51	0.32	0.82	0.51	0.46
u(xi)	3.71	1.22	2.89	1.0	1.2	4.3	1.4	3.6	2.5	1.85
U(xi)	7.42	2.4	5.78	2.0	2.4	8.6	2.8	7.3	5.0	3.7

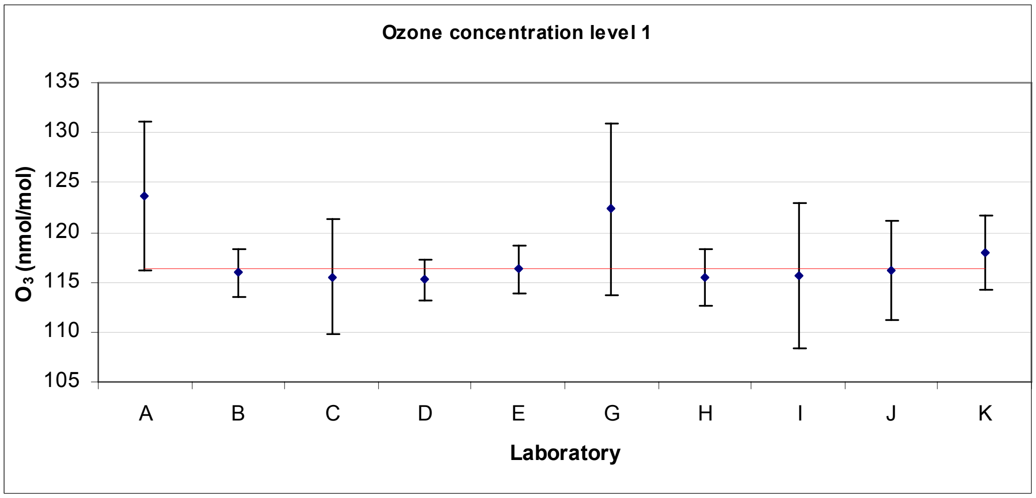

Figure 26: Reported values for O3 concentration level 1.

Table 21: Reported values for O3 concentration level 2.

parameter: O3	all units are nmol/mol									
level: 2	x*: 100.53		s*: 0.98							
	A	B	C	D	E	G	H	I	J	K
xi,1	106.50	99.89	100.0	99.2	100.0	105.6	99.5	99.2	100.0	101.9
xi,2	107.00	100.20	100.7	99.7	100.3	106.2	99.9	99.6	100.5	102.2
xi,3	107.20	100.40	100.7	99.9	100.5	106.4	100.0	99.8	100.6	102.4
xi	106.900	100.163	100.47	99.60	100.27	106.07	99.80	99.53	100.37	102.17
si	0.361	0.257	0.40	0.36	0.25	0.42	0.26	0.31	0.32	0.25
u(xi)	3.20	1.06	2.51	0.9	1.0	3.7	1.2	3.3	2.3	1.6
U(xi)	6.40	2.1	5.02	1.7	2.0	7.5	2.5	6.7	4.6	3.2

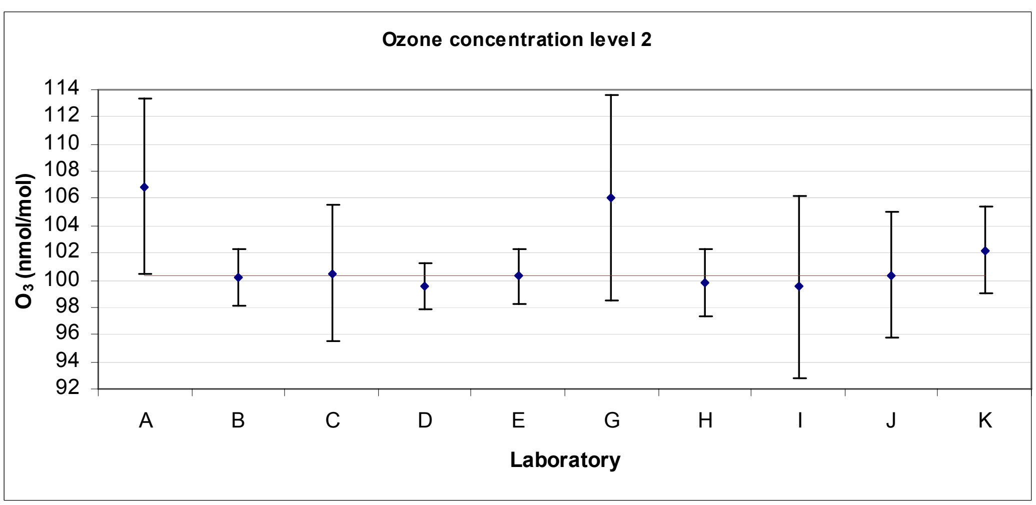

Figure 27: Reported values for O3 concentration level 2.

Table 22: Reported values for O3 concentration level 3.

parameter: O3 level: 3 — all units are nmol/mol — x*: 60.15 s*: 0.52

	A	B	C	D	E	G	H	I	J	K
xi,1	63.90	60.04	60.2	59.6	59.8	63.9	59.9	59.6	59.7	61.4
xi,2	64.00	60.07	60.3	59.6	59.9	64.0	59.9	59.6	59.9	61.6
xi,3	64.00	60.09	60.4	59.6	59.9	64.0	60.0	59.7	59.9	61.5
xi	63.967	60.067	60.30	59.60	59.87	63.97	59.93	59.63	59.83	61.50
si	0.058	0.025	0.10	0.00	0.06	0.06	0.06	0.06	0.12	0.10
u(xi)	2.20	1.05	1.51	0.5	1.0	2.2	1.1	2.7	1.9	0.95
U(xi)	4.50	2.1	3.02	1.0	2.0	4.5	2.3	5.4	3.8	1.91

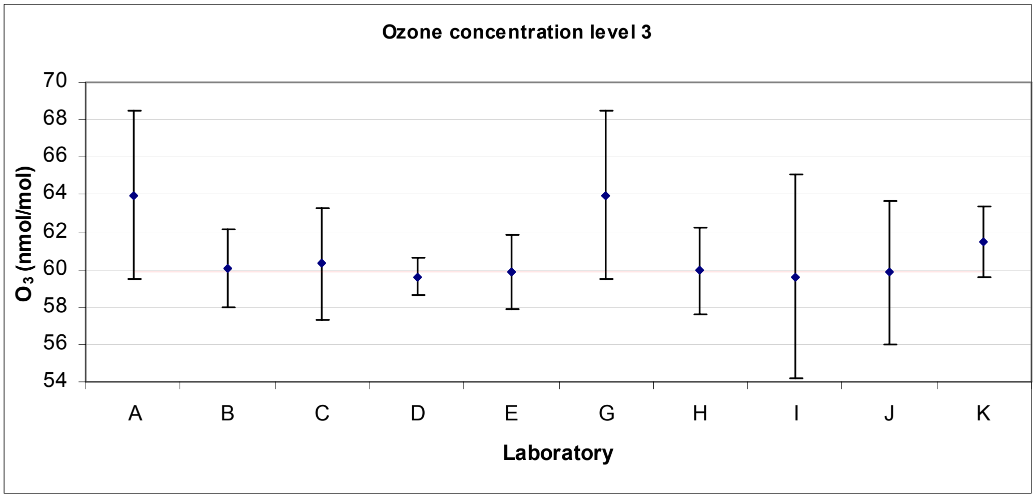

Figure 28: Reported values for O3 concentration level 3.

Table 23: Reported values for O3 concentration level 4.

parameter: O3 level: 4 — all units are nmol/mol — x*: 22.20 s*: 0.51

	A	B	C	D	E	G	H	I	J	K
xi,1	23.60	22.21	22.1	21.9	21.7	24.2	22.2	21.9	21.5	23.1
xi,2	23.60	21.98	22.2	22.0	21.8	24.2	22.1	22.0	21.5	22.9
xi,3	23.60	22.14	22.2	21.9	21.8	24.2	22.2	21.9	21.6	23.0
xi	23.600	22.110	22.17	21.93	21.77	24.20	22.17	21.93	21.53	23.00
si	0.000	0.118	0.06	0.06	0.06	0.00	0.06	0.06	0.06	0.10
u(xi)	0.80	1.05	0.55	0.2	1.0	0.9	1.1	2.3	1.5	0.9
U(xi)	1.60	2.1	1.11	0.4	2.0	1.7	2.3	4.5	3.0	1.8

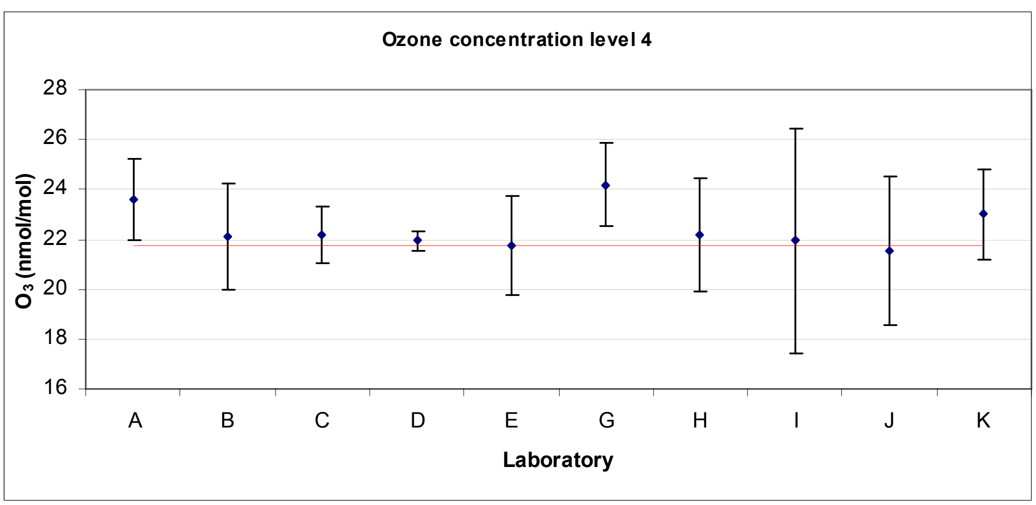

Figure 29: Reported values for O3 concentration level 4.

Table 24: Reported values for O3 concentration level 5.

parameter: O3			all units are nmol/mol							
level: 5			x*: 14.59		s*: 0.39					
	A	B	C	D	E	G	H	I	J	K
xi,1	14.90	14.64	14.5	14.4	14.2	16.3	14.6	14.5	13.8	15.5
xi,2	14.90	14.68	14.3	14.4	14.2	16.3	14.6	14.5	14.0	15.5
xi,3	14.80	14.70	14.6	14.4	14.2	16.2	14.6	14.5	14.0	15.4
xi	14.867	14.673	14.47	14.40	14.20	16.27	14.60	14.50	13.93	15.47
si	0.058	0.031	0.15	0.00	0.00	0.06	0.00	0.00	0.12	0.06
u(xi)	0.50	1.05	0.36	0.1	1.0	0.6	1.1	2.2	1.4	0.9
U(xi)	1.20	2.1	0.72	0.2	2.0	1.2	2.3	4.4	2.8	1.8

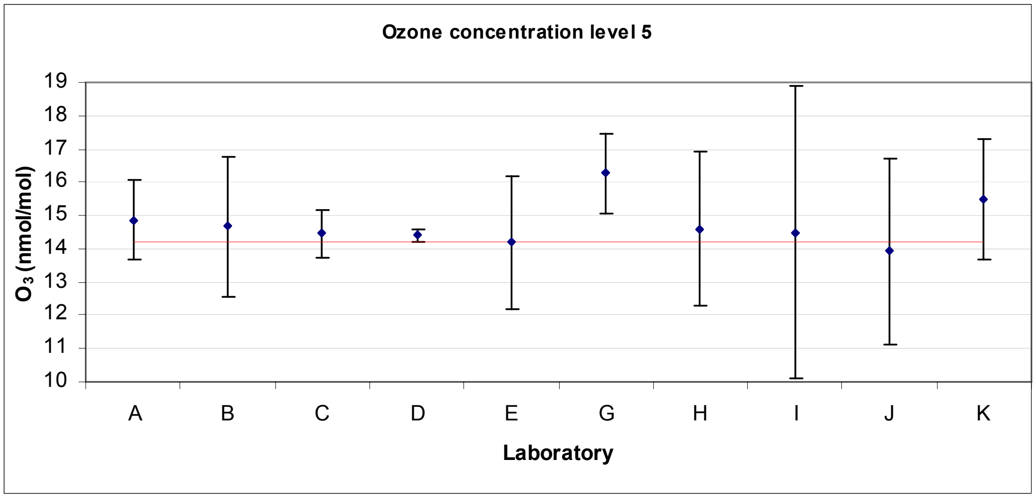

Figure 30: Reported values for O3 concentration level 5.

Reported values for NO

Table 25: Reported values for NO concentration level 0.

parameter: NO			all units are nmol/mol							
level: 0			x*: 0.1		s*: 0.2					
	A	B	C	D	E	G	H	I	J	K
xi,1	0.10	0.1	0.0	0.2	0.4	-0.4	0.0	0.2	0.0	0.3
u(xi)	0.006	0.82	0.08	0.0	0.3	0.1	0.5	0.9		1.3
U(xi)	0.012	1.6	0.16	0.0	0.6	0.2	1.1	1.8		2.6

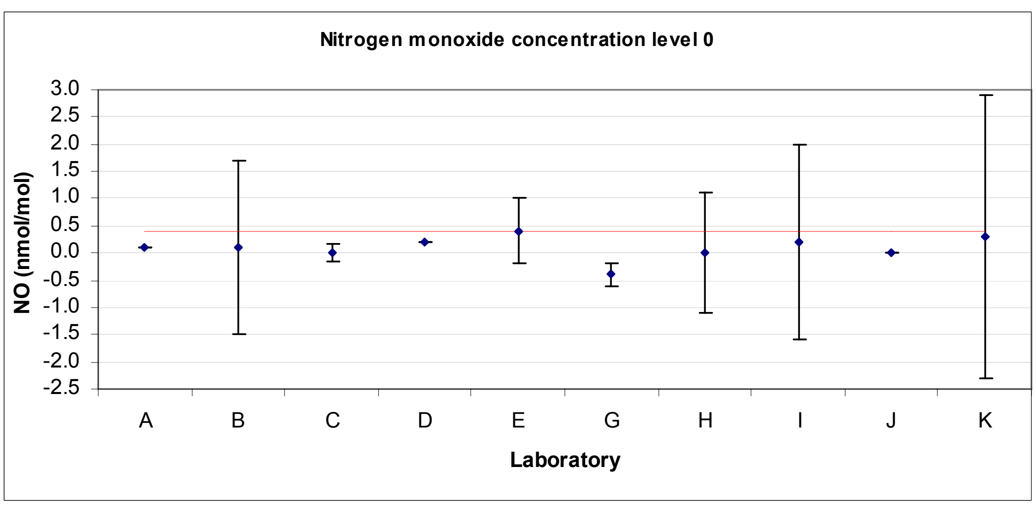

Figure 31: Reported values for NO concentration level 0.

Table 26: Reported values for NO concentration level 1.

parameter: NO	all units are nmol/mol									
level: 1	x*: 503.83		s*: 3.43							
	A	B	C	D	E	G	H	I	J	K
xi,1	502.40	513.60	504.1	487.8	501.4	521.7	500.8	509.3	502.89	503.0
xi,2	503.00	513.37	504.6	488.0	501.9	522.6	500.9	509.3	503.76	503.5
xi,3	502.70	511.83	505.0	488.1	502.1	522.7	500.9	509.3	503.96	502.6
xi	502.700	512.933	504.57	487.97	501.80	522.33	500.87	509.30	503.537	503.03
si	0.300	0.962	0.45	0.15	0.36	0.55	0.06	0.00	0.569	0.45
u(xi)	17.60	4.74	7.57	11.7	1.7	13.5	10.4	15.8	7.80	8.8
U(xi)	35.20	9.5	15.14	23.4	3.4	27.0	20.8	31.6	15.60	17.6

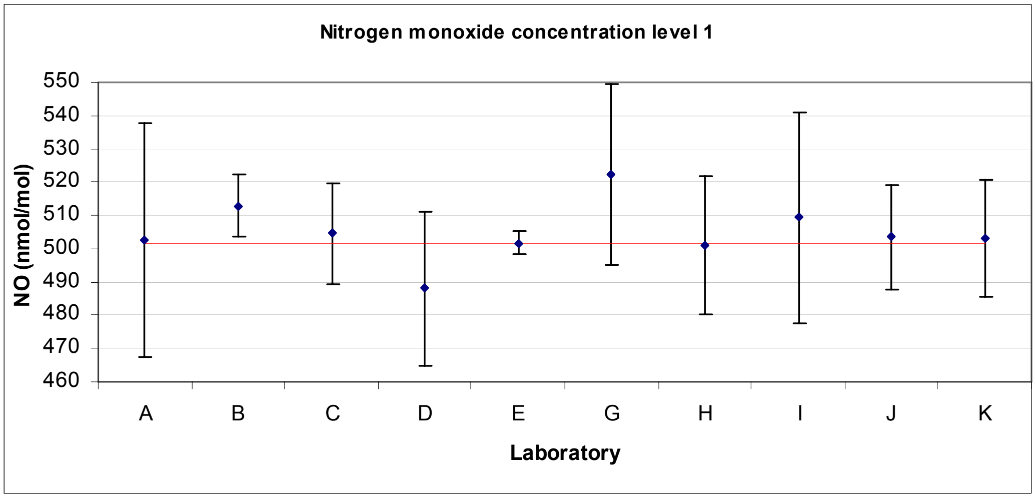

Figure 32: Reported values for NO concentration level 1.

Table 27: Reported values for NO concentration level 2.

parameter: NO	all units are nmol/mol									
level: 2	x*: 385.07		s*: 4.71							
	A	B	C	D	E	G	H	I	J	K
xi,1	384.60	388.59	387.3	373.8	383.6	399.6	382.7	390.8	384.19	381.5
xi,2	384.90	388.43	387.1	373.5	383.0	399.0	382.7	390.8	383.98	381.6
xi,3	384.50	388.33	387.0	373.4	382.8	398.8	382.2	390.4	383.85	380.9
xi	384.667	388.450	387.13	373.57	383.13	399.13	382.53	390.67	384.007	381.33
si	0.208	0.131	0.15	0.21	0.42	0.42	0.29	0.23	0.172	0.38
u(xi)	13.50	3.63	5.81	9.0	1.4	10.3	7.9	12.1	6.05	6.65
U(xi)	27.00	7.3	11.6	17.9	2.7	20.6	15.9	24.3	12.10	13.3

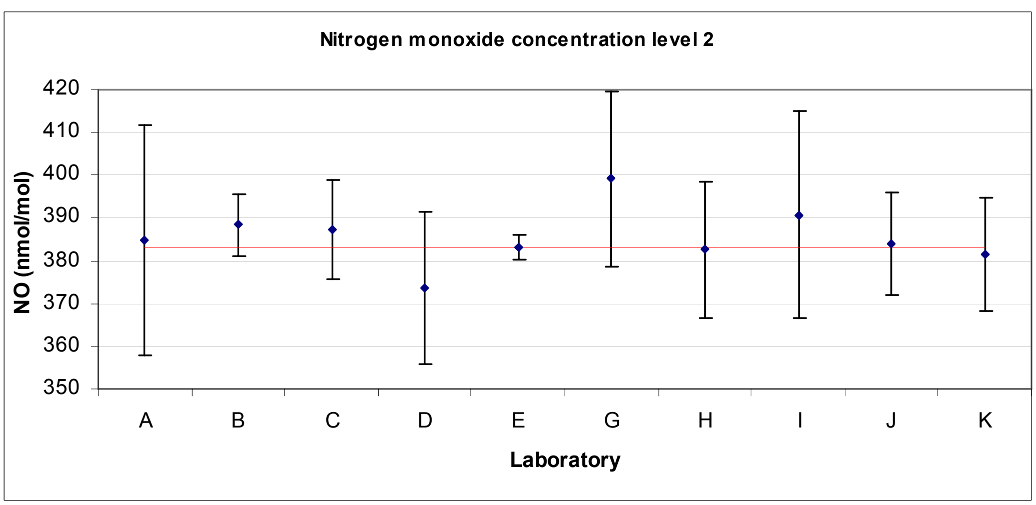

Figure 33: Reported values for NO concentration level 2.

Table 28: Reported values for NO concentration level 3.

parameter: NO	all units are nmol/mol									
level: 3	x*: 251.33		s*: 4.67							
	A	B	C	D	E	G	H	I	J	K
xi,1	250.40	255.08	252.4	244.4	250.8	256.7	246.9	254.7	250.49	245.5
xi,2	251.00	255.41	253.0	244.9	251.5	257.6	247.4	255.5	251.91	246.7
xi,3	251.40	255.59	253.5	245.0	251.6	257.4	247.6	255.6	252.84	247.1
xi	250.933	255.360	252.97	244.77	251.30	257.23	247.30	255.27	251.747	246.43
si	0.503	0.259	0.55	0.32	0.44	0.47	0.36	0.49	1.183	0.83
u(xi)	8.80	2.47	3.79	5.9	1.1	6.7	5.1	7.9	4.29	4.3
U(xi)	17.60	4.9	7.59	11.7	2.2	13.3	10.3	15.9	8.58	8.6

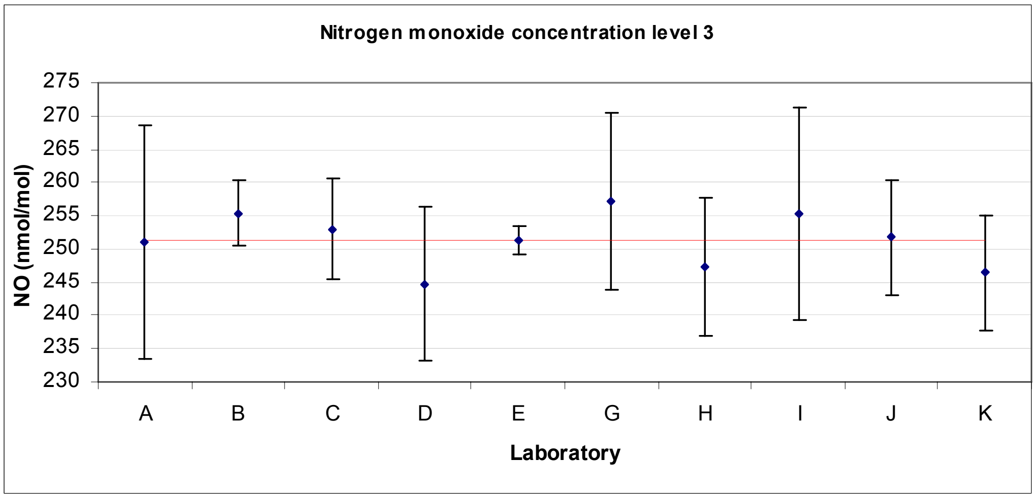

Figure 34: Reported values for NO concentration level 3.

Table 29: Reported values for NO concentration level 4.

parameter: NO	all units are nmol/mol									
level: 4	x*: 151.35		s*: 2.90							
	A	B	C	D	E	G	H	I	J	K
xi,1	151.00	153.08	152.7	147.5	151.2	154.9	148.7	155.0	151.47	148.9
xi,2	150.90	153.01	152.4	147.4	151.1	154.7	148.7	155.2	151.61	148.9
xi,3	150.80	152.89	152.0	147.2	150.9	154.5	148.7	155.1	151.40	148.6
xi	150.900	152.993	152.37	147.37	151.07	154.70	148.70	155.10	151.493	148.80
si	0.100	0.096	0.35	0.15	0.15	0.20	0.00	0.10	0.107	0.17
u(xi)	5.30	1.62	2.29	3.5	0.7	4.0	3.1	4.9	2.66	2.6
U(xi)	10.50	3.2	4.57	7.1	1.4	8.0	6.2	9.8	5.32	5.2

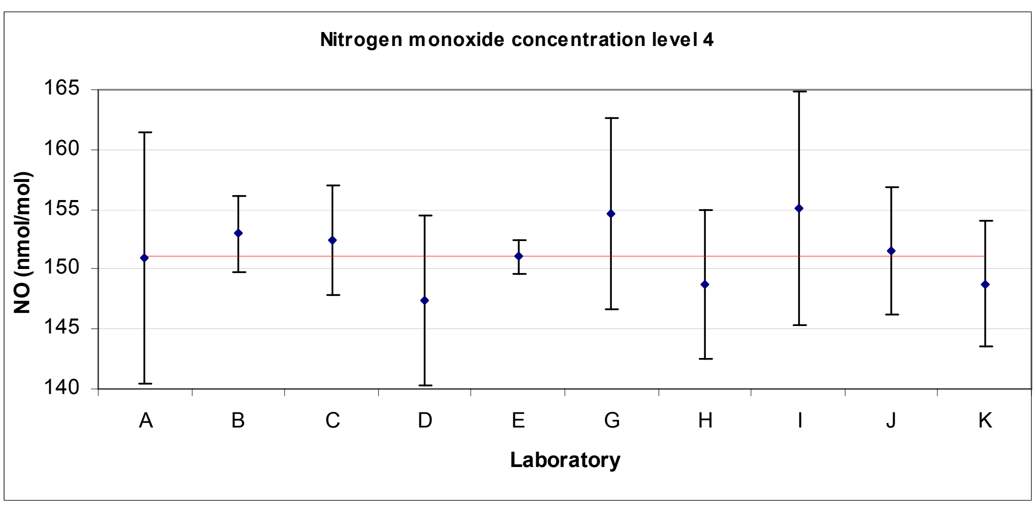

Figure 35: Reported values for NO concentration level 4.

Table 30: Reported values for NO concentration level 5.

parameter: NO, level: 5 — all units are nmol/mol — x*: 150.39 s*: 2.58

	A	B	C	D	E	G	H	I	J	K
xi,1	149.00	152.48	150.7	146.2	150.7	152.4	148.2	153.1	150.97	146.8
xi,2	149.80	152.88	151.0	146.5	151.0	152.7	148.4	153.3	151.37	147.5
xi,3	150.10	152.72	151.0	146.4	151.0	152.9	148.4	153.3	151.66	147.4
xi	149.633	152.693	150.90	146.37	150.90	152.67	148.33	153.23	151.333	147.23
si	0.569	0.201	0.17	0.15	0.17	0.25	0.12	0.12	0.346	0.38
u(xi)	5.20	1.62	2.26	3.5	0.7	4.0	3.1	4.8	2.68	2.6
U(xi)	10.50	3.2	4.53	7.0	1.4	8.0	6.2	9.7	5.36	5.2

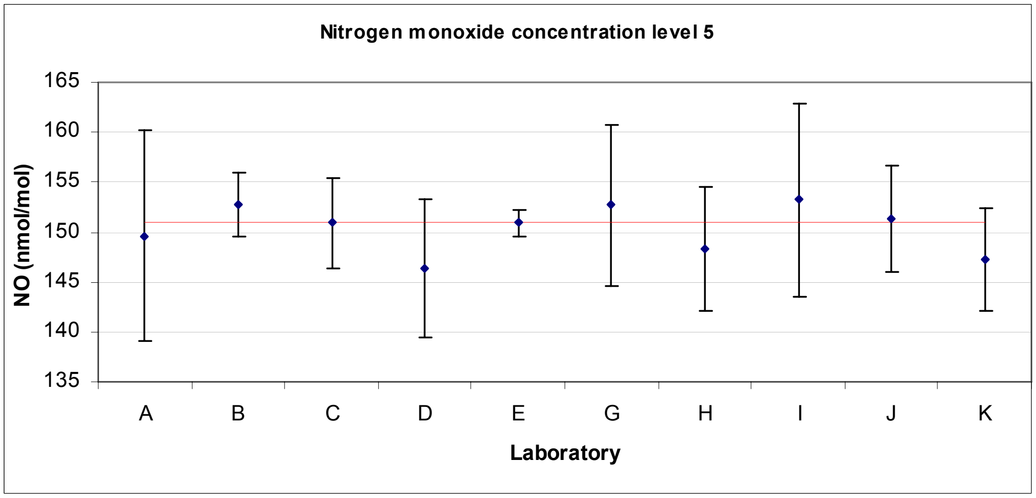

Figure 36: Reported values for NO concentration level 5.

Table 31: Reported values for NO concentration level 6.

parameter: NO, level: 6 — all units are nmol/mol — x*: 90.14 s*: 1.65

	A	B	C	D	E	G	H	I	J	K
xi,1	89.60	91.36	90.7	87.8	90.4	91.9	88.6	92.5	90.60	88.9
xi,2	89.50	91.21	90.4	87.8	90.4	91.6	88.6	92.6	90.55	88.7
xi,3	89.40	91.06	90.4	87.7	90.2	91.6	88.6	92.3	90.45	88.3
xi	89.500	91.210	90.50	87.77	90.33	91.70	88.60	92.47	90.533	88.63
si	0.100	0.150	0.17	0.06	0.12	0.17	0.00	0.15	0.076	0.31
u(xi)	3.50	1.17	1.36	2.1	0.5	2.4	1.8	3.0	1.78	1.55
U(xi)	7.10	2.3	2.72	4.2	1.0	4.8	3.7	6.0	3.56	3.1

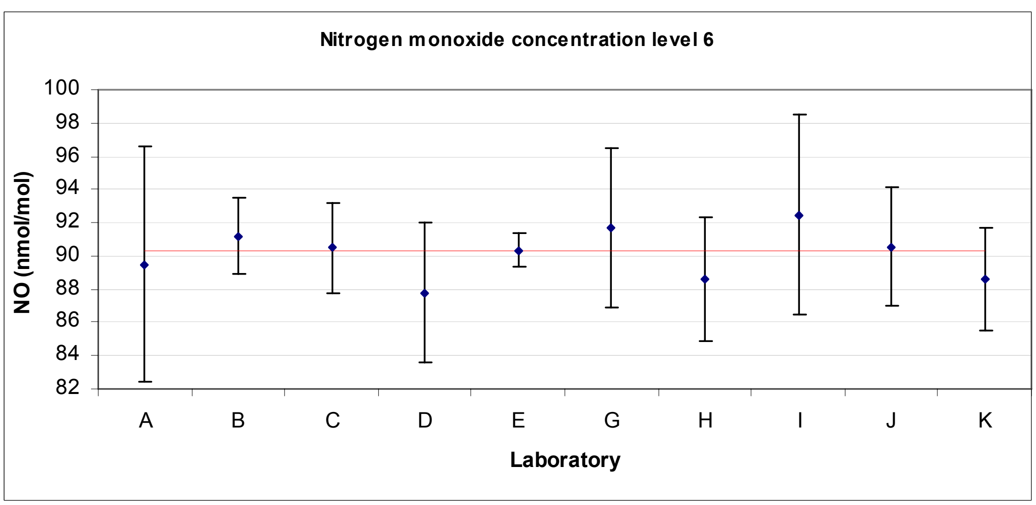

Figure 37: Reported values for NO concentration level 6.

Table 32: Reported values for NO concentration level 7.

parameter: NO all units are nmol/mol
level: 7 x*: 50.13 s*: 1.11

	A	B	C	D	E	G	H	I	J	K
xi,1	49.00	51.26	50.3	49.0	50.8	50.5	49.5	51.3	50.36	48.8
xi,2	49.00	51.30	50.6	49.1	51.0	50.6	49.5	51.4	50.42	48.7
xi,3	49.00	51.33	50.4	49.0	51.0	50.7	49.5	51.3	50.51	48.8
xi	49.000	51.297	50.43	49.03	50.93	50.60	49.50	51.33	50.430	48.77
si	0.000	0.035	0.15	0.06	0.12	0.10	0.00	0.06	0.075	0.06
u(xi)	1.88	0.94	0.76	1.2	0.4	1.3	1.1	1.8	1.19	1.3
U(xi)	3.76	1.9	1.51	2.4	0.8	2.6	2.3	3.7	2.38	2.6

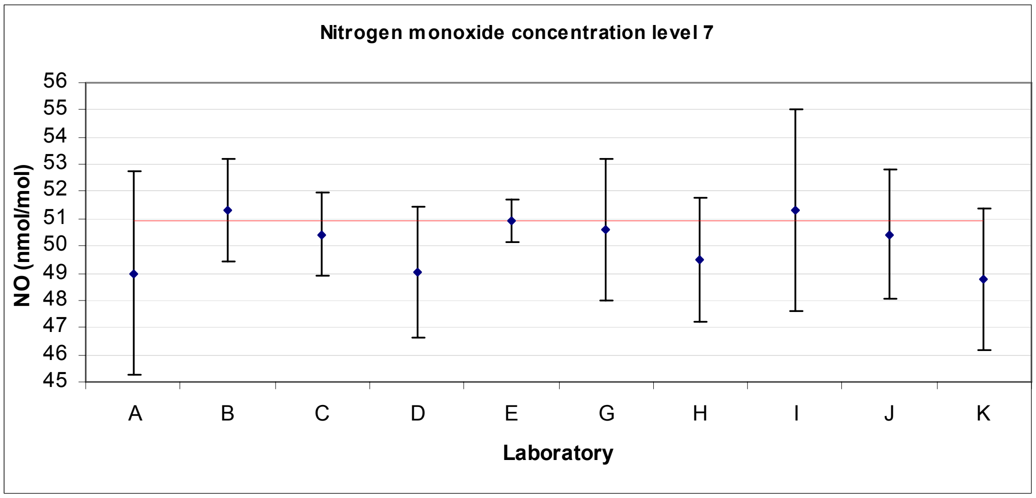

Figure 38: Reported values for NO concentration level 7.

Table 33: Reported values for NO concentration level 8.

parameter: NO all units are nmol/mol
level: 8 x*: 28.32 s*: 0.68

	A	B	C	D	E	G	H	I	J	K
xi,1	27.70	28.91	28.6	27.7	28.9	28.8	27.6	29.3	28.52	27.9
xi,2	27.60	28.78	28.5	27.7	28.9	28.7	27.6	29.2	28.37	27.9
xi,3	27.40	28.76	28.6	27.5	28.7	28.7	27.6	29.0	28.30	27.8
xi	27.567	28.817	28.57	27.63	28.83	28.73	27.60	29.17	28.397	27.87
si	0.153	0.081	0.06	0.12	0.12	0.06	0.00	0.15	0.112	0.06
u(xi)	1.24	0.86	0.43	0.7	0.3	0.7	0.8	1.3	0.88	1.3
U(xi)	2.50	1.7	0.86	1.3	0.7	1.5	1.6	2.6	1.76	2.6

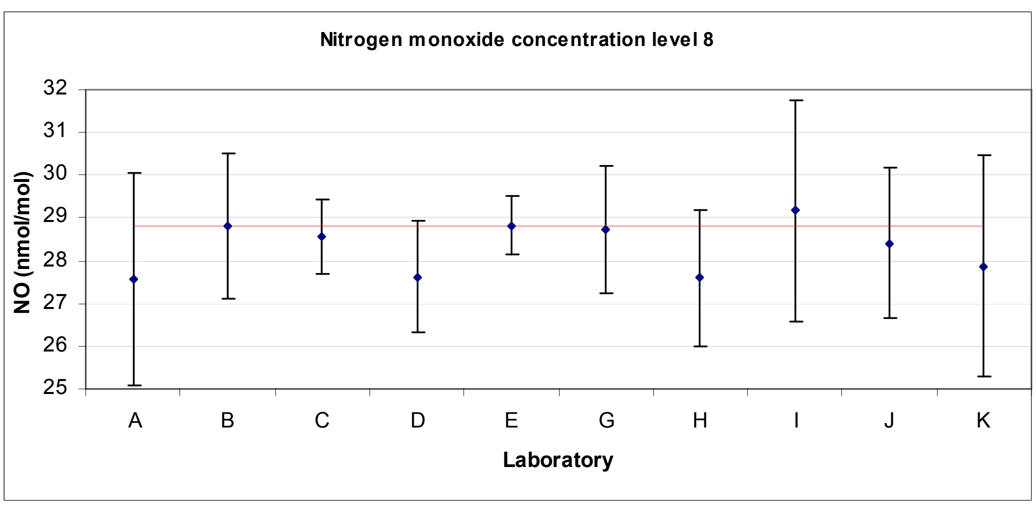

Figure 39: Reported values for NO concentration level 8.

Table 34: Reported values for NO concentration level 9.

parameter: NO	all units are nmol/mol									
level: 9	x*: 15.21		s*: 0.50							
	A	B	C	D	E	G	H	I	J	K
xi,1	14.10	15.31	15.3	14.5	15.3	14.6	14.6	15.2	14.45	14.7
xi,2	14.70	15.86	15.5	15.1	16.0	15.5	15.0	15.9	15.01	14.8
xi,3	14.80	15.92	15.8	15.2	16.0	15.7	15.3	15.9	15.10	15.0
xi	14.533	15.697	15.53	14.93	15.77	15.27	14.97	15.67	14.853	14.83
si	0.379	0.336	0.25	0.38	0.40	0.59	0.35	0.40	0.352	0.15
u(xi)	0.58	0.83	0.22	0.4	0.6	0.8	0.6	1.1	0.76	1.3
U(xi)	1.20	1.7	0.45	0.7	1.2	1.6	1.3	2.2	1.52	2.6

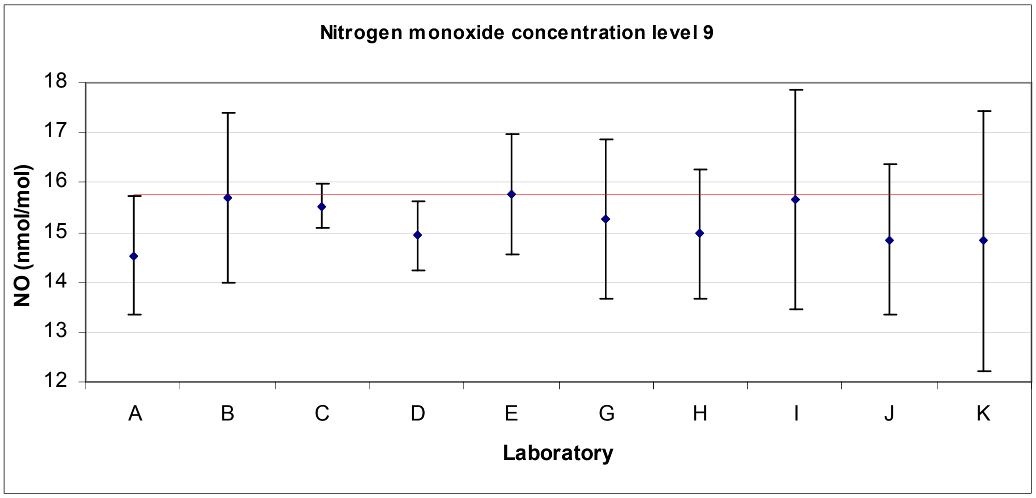

Figure 40: Reported values for NO concentration level 9.

Table 35: Reported values for NO concentration level 10.

parameter: NO	all units are nmol/mol									
level: 10	x*: 1.71		s*: 0.27							
	A	B	C	D	E	G	H	I	J	K
xi,1	1.30	1.79	1.7	1.9	2.0	2.0	1.5	2.0	1.64	2.0
xi,2	1.20	1.69	1.7	1.7	2.0	2.0	1.3	2.0	1.57	1.8
xi,3	1.20	1.60	1.4	1.7	1.9	1.9	1.3	1.8	1.47	1.8
xi	1.233	1.693	1.60	1.77	1.97	1.97	1.37	1.93	1.560	1.87
si	0.058	0.095	0.17	0.12	0.06	0.06	0.12	0.12	0.085	0.12
u(xi)	0.05	0.82	0.02	0.0	0.3	0.1	0.5	0.9		1.3
U(xi)	0.10	1.6	0.05	0.1	0.7	0.2	1.1	1.9		2.6

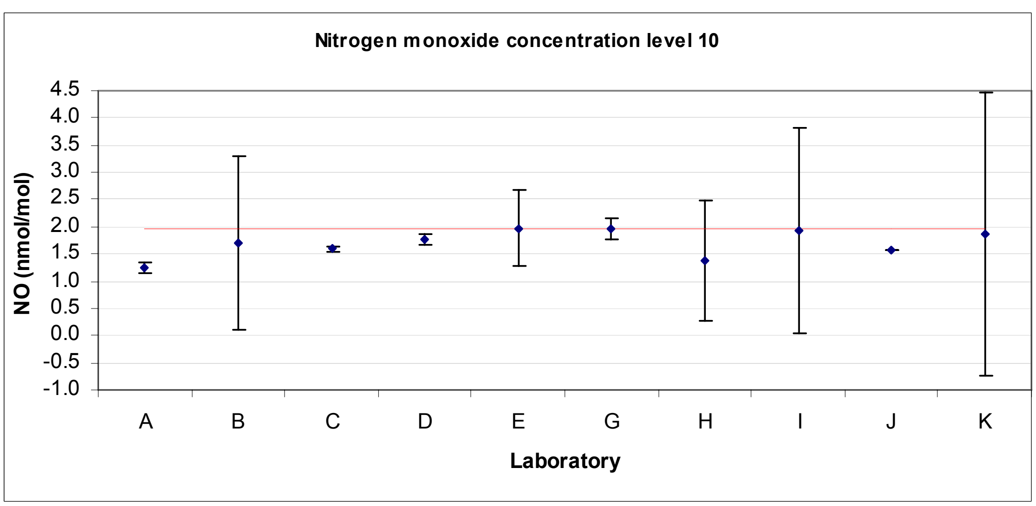

Figure 41: Reported values for NO concentration level 10.

Reported values for NO_2

Table 36: Reported values for NO_2 concentration level 0.

parameter: NO2	all units are nmol/mol									
level: 0	x*: 0.1		s*: 0.2							
	A	B	C	D	E	G	H	I	J	K
xi,1	0.10	0.0	0.4	0.1	0.1	-1.6	0.3	0.0	0.0	0.3
u(xi)	0.006	0.82	0.15	0.0	0.1	0.1	0.5	1.8		1.55
U(xi)	0.012	1.6	0.30	0.0	0.2	0.3	1.1	3.6		3.1

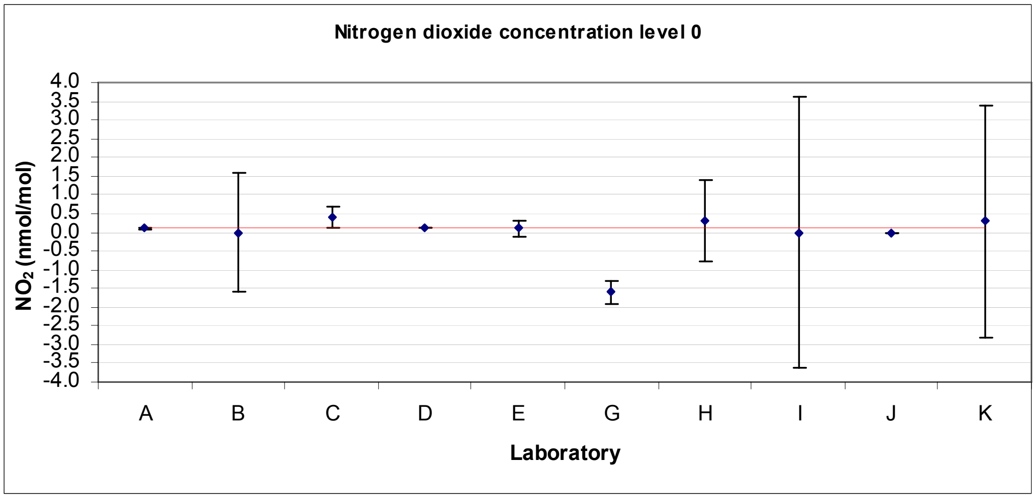

Figure 42: Reported values for NO_2 concentration level 0.

Table 37: Reported values for NO_2 concentration level 1.

parameter: NO2	all units are nmol/mol									
level: 1	x*: 1.9		s*: 2.3							
	A	B	C	D	E	G	H	I	J	K
xi,1	-1.0	0.50	2.6	1.9	-0.1	4.3	2.4	0.0	4.95	3.3
xi,2	-1.0	1.05	3.0	1.8	-0.6	3.8	2.4	0.1	4.65	3.2
xi,3	-1.5	0.76	3.5	1.9	-0.6	5.1	2.4	0.0	4.41	3.1
xi	-1.17	0.770	3.03	1.87	-0.43	4.40	2.40	0.03	4.670	3.20
si	0.29	0.275	0.45	0.06	0.29	0.66	0.00	0.06	0.271	0.10
u(xi)	0.03	0.82	0.05	0.0	0.9	0.8	0.6	20.6		1.55
U(xi)	0.06	1.6	0.09	0.1	1.8	1.7	1.2	41.3		3.1

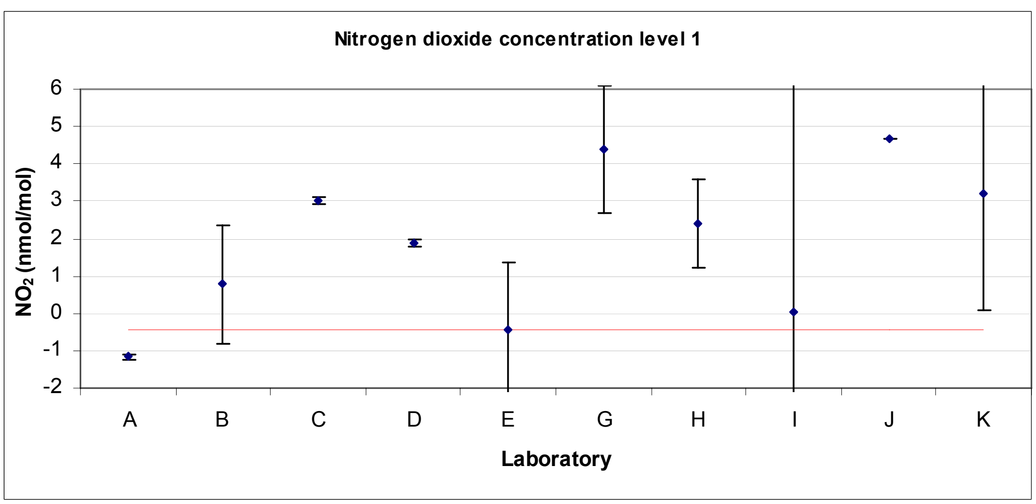

Figure 43: Reported values for NO_2 concentration level 1.

Table 38: Reported values for NO_2 concentration level 2.

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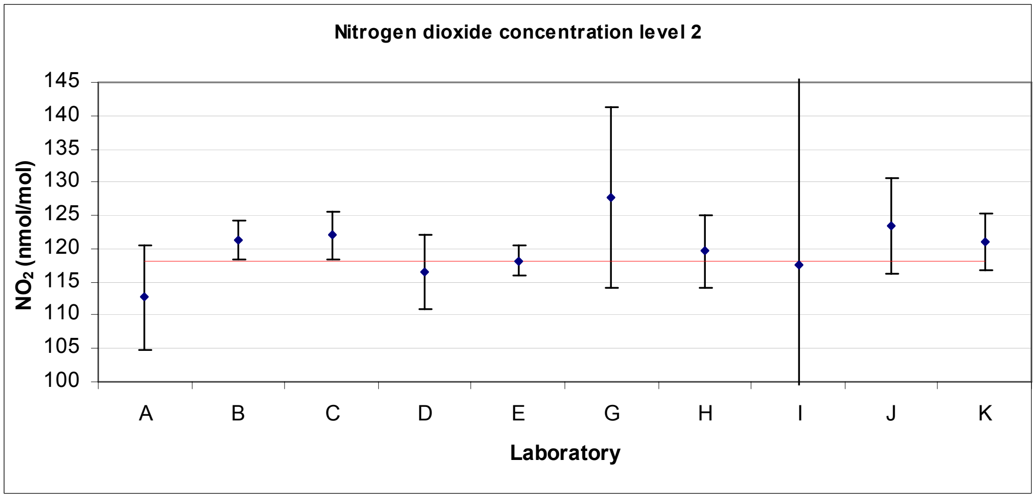

Figure 44: Reported values for NO_2 concentration level 2.

Table 39: Reported values for NO_2 concentration level 3.

parameter: NO2	all units are nmol/mol									
level: 3	x*: 1.6	s*: 1.1								
	A	B	C	D	E	G	H	I	J	K
xi,1	0.5	0.96	1.9	1.6	0.3	2.8	1.7	0.7	3.28	3.1
xi,2	1.0	0.96	2.0	1.4	0.0	2.3	1.9	0.5	2.67	2.9
xi,3	1.0	0.78	1.9	1.4	-0.1	2.4	1.7	0.4	2.45	3.1
xi	0.83	0.900	1.93	1.47	0.07	2.50	1.77	0.53	2.800	3.03
si	0.29	0.104	0.06	0.12	0.21	0.26	0.12	0.15	0.430	0.12
u(xi)	0.025	0.82	0.03	0.0	0.9	0.5	0.5	10.4		1.55
U(xi)	0.05	1.6	0.06	0.1	1.8	0.9	1.1	20.9		3.1

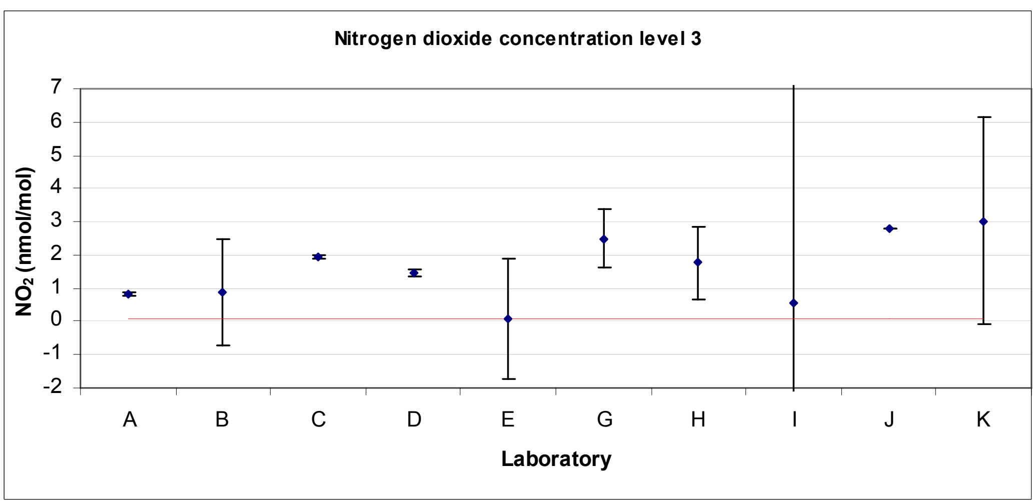

Figure 45: Reported values for NO_2 concentration level 3.

Table 40: Reported values for NO_2 concentration level 4.

parameter: NO2 — level: 4 — all units are nmol/mol — x*: 101.61 — s*: 2.38

	A	B	C	D	E	G	H	I	J	K
xi,1	97.60	103.45	102.0	99.1	101.0	104.5	99.9	101.0	103.89	101.6
xi,2	97.70	103.54	102.7	99.1	100.9	104.5	100.2	101.1	103.71	101.8
xi,3	98.00	103.71	102.6	99.5	101.3	104.9	100.7	101.3	104.05	102.1
xi	97.767	103.567	102.43	99.23	101.07	104.63	100.27	101.13	103.883	101.83
si	0.208	0.132	0.38	0.23	0.21	0.23	0.40	0.15	0.170	0.25
u(xi)	3.40	1.34	1.54	2.4	0.9	5.6	2.3	8.8	3.05	1.8
U(xi)	6.80	2.7	3.07	4.8	1.8	11.1	4.6	17.7	6.10	3.6

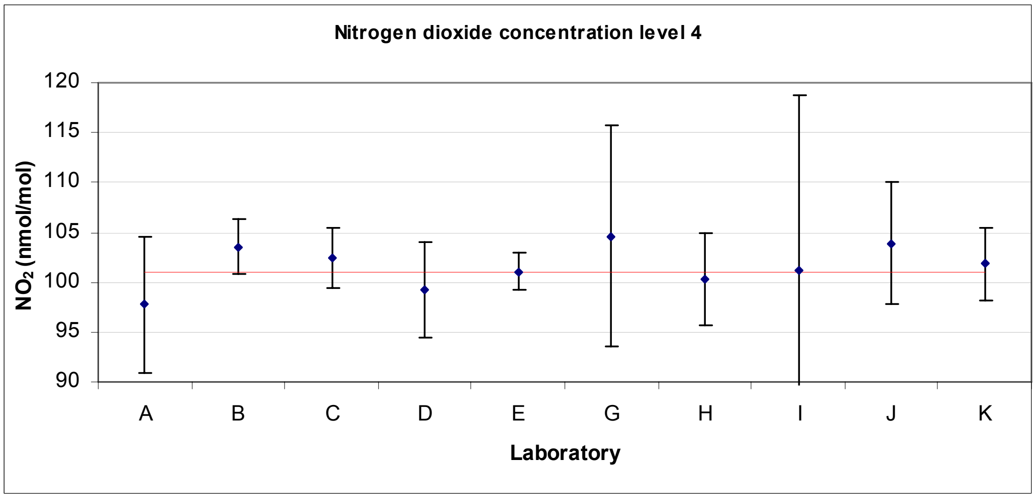

Figure 46: Reported values for NO_2 concentration level 4.

Table 41: Reported values for NO_2 concentration level 5.

parameter: NO2 — level: 5 — all units are nmol/mol — x*: 0.6 — s*: 0.4

	A	B	C	D	E	G	H	I	J	K
xi,1	1.0	0.35	0.6	0.6	-0.3	0.5	0.8	-0.1	1.19	0.7
xi,2	1.0	0.14	0.8	0.6	-0.3	0.8	0.8	-0.1	1.18	0.7
xi,3	1.0	0.41	0.7	0.6	-0.1	0.5	0.8	-0.1	1.13	0.6
xi	1.00	0.300	0.70	0.60	-0.23	0.60	0.80	-0.10	1.167	0.67
si	0.00	0.142	0.10	0.00	0.12	0.17	0.00	0.00	0.032	0.06
u(xi)	0.028	0.82	0.005	0.0	0.5	0.3	0.5	6.3		1.55
U(xi)	0.06	1.6	0.01	0.0	1.0	0.5	1.1	12.7		3.1

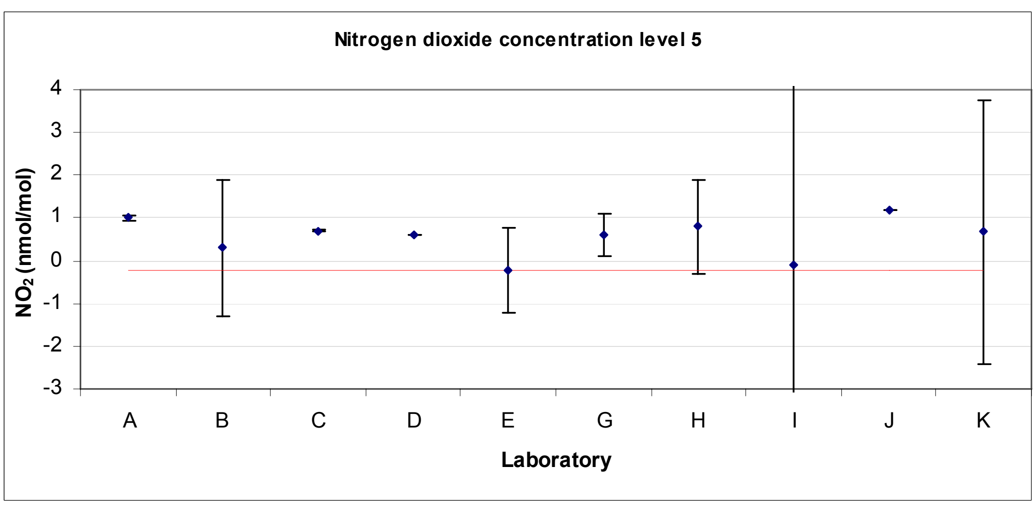

Figure 47: Reported values for NO_2 concentration level 5.

Table 42: Reported values for NO_2 concentration level 6.

parameter: NO2 — level: 6 — all units are nmol/mol — x*: 60.51 — s*: 1.13

	A	B	C	D	E	G	H	I	J	K
xi,1	58.40	61.85	60.5	59.1	60.4	61.0	60.1	60.4	61.84	59.7
xi,2	58.40	61.93	60.6	59.3	60.5	61.4	60.1	60.5	61.99	59.9
xi,3	58.50	62.14	60.6	59.3	60.6	61.4	60.1	60.6	62.31	60.3
xi	58.433	61.973	60.57	59.23	60.50	61.27	60.10	60.50	62.047	59.97
si	0.058	0.150	0.06	0.12	0.10	0.23	0.00	0.10	0.240	0.31
u(xi)	2.30	1.03	0.91	1.4	0.6	3.3	1.4	5.4	1.95	1.55
U(xi)	4.70	2.1	1.82	2.8	1.1	6.5	2.9	10.9	3.90	3.1

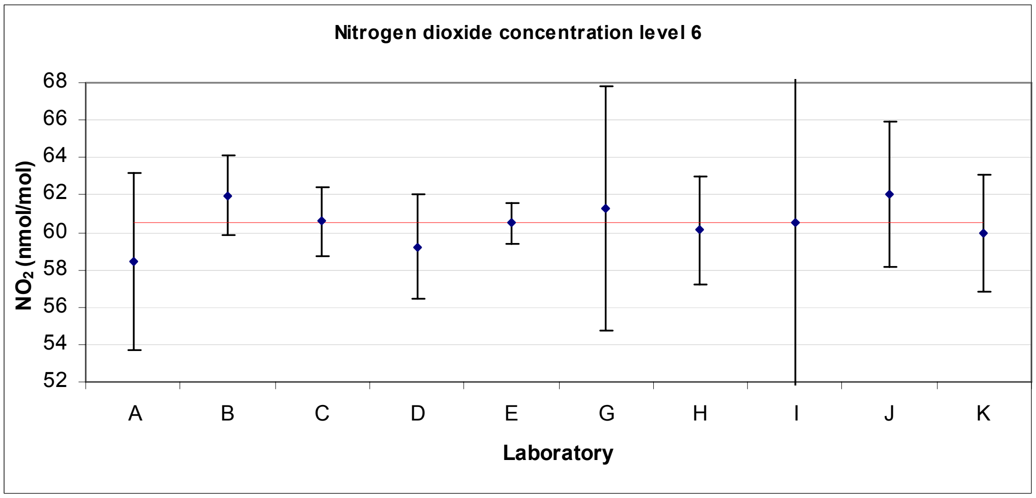

Figure 48: Reported values for NO_2 concentration level 6.

Table 43: Reported values for NO_2 concentration level 7.

parameter: NO2 — level: 7 — all units are nmol/mol — x*: 0.3 — s*: 0.3

	A	B	C	D	E	G	H	I	J	K
xi,1	0.5	0.13	0.2	0.3	0.1	-0.8	0.5	0.1	0.37	0.7
xi,2	0.5	0.12	0.5	0.2	-0.1	-0.8	0.5	0.0	0.41	0.7
xi,3	0.6	0.11	0.4	0.3	0.0	-0.9	0.5	-0.1	0.38	0.6
xi	0.53	0.120	0.37	0.27	0.00	-0.83	0.50	0.00	0.387	0.67
si	0.06	0.010	0.15	0.06	0.10	0.06	0.00	0.10	0.021	0.06
u(xi)	0.015	0.82	0.001	0.0	0.3	0.1	0.5	2.6		1.55
U(xi)	0.03	1.6	0.003	0.0	0.6	0.3	1.1	5.3		3.1

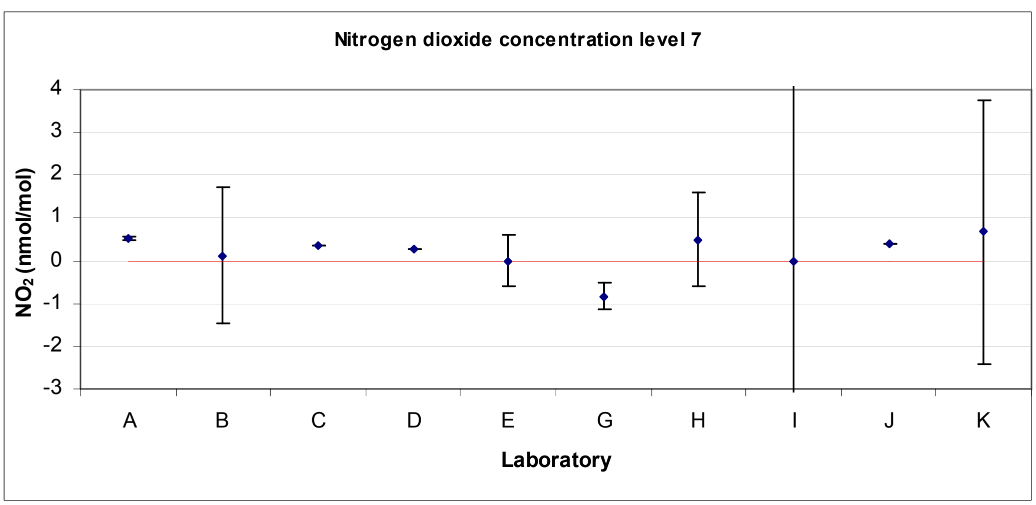

Figure 49: Reported values for NO_2 concentration level 7.

Table 44: Reported values for NO_2 concentration level 8.

parameter: NO2	all units are nmol/mol									
level: 8	x*: 21.81	s*: 0.66								
	A	B	C	D	E	G	H	I	J	K
xi,1	21.20	22.67	21.3	21.5	22.1	20.8	22.1	21.9	22.36	21.6
xi,2	21.20	22.76	21.6	21.6	22.2	20.9	22.3	22.1	22.44	21.3
xi,3	21.30	22.72	21.2	21.7	22.2	21.1	22.3	22.1	22.44	21.4
xi	21.233	22.717	21.37	21.60	22.17	20.93	22.23	22.03	22.413	21.43
si	0.058	0.045	0.21	0.10	0.06	0.15	0.12	0.12	0.046	0.15
u(xi)	0.96	0.85	0.32	0.5	0.3	1.1	0.7	2.4	0.89	1.55
U(xi)	1.90	1.7	0.64	1.0	0.6	2.2	1.5	4.8	1.78	3.1

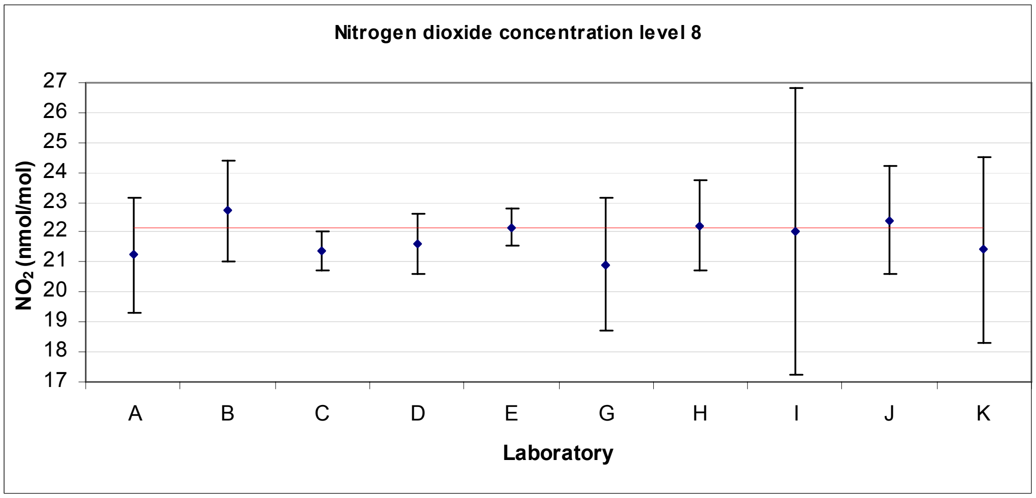

Figure 50: Reported values for NO_2 concentration level 8.

Table 45: Reported values for NO_2 concentration level 9.

parameter: NO2	all units are nmol/mol									
level: 9	x*: 0.3	s*: 0.1								
	A	B	C	D	E	G	H	I	J	K
xi,1	0.5	0.35	0.4	0.4	0.3	-1.1	0.5	0.4	0.40	0.4
xi,2	0.5	0.05	0.1	0.2	0.1	-1.2	0.3	0.0	0.39	0.3
xi,3	0.6	0.12	0.4	0.1	0.1	-1.6	0.3	0.0	0.28	0.1
xi	0.53	0.173	0.30	0.23	0.17	-1.30	0.37	0.13	0.357	0.27
si	0.06	0.157	0.17	0.15	0.12	0.26	0.12	0.23	0.067	0.15
u(xi)	0.015	0.82	0.005	0.0	0.6	0.3	0.5	1.8		1.55
U(xi)	0.03	1.6	0.01	0.0	1.3	0.5	1.1	3.7		3.1

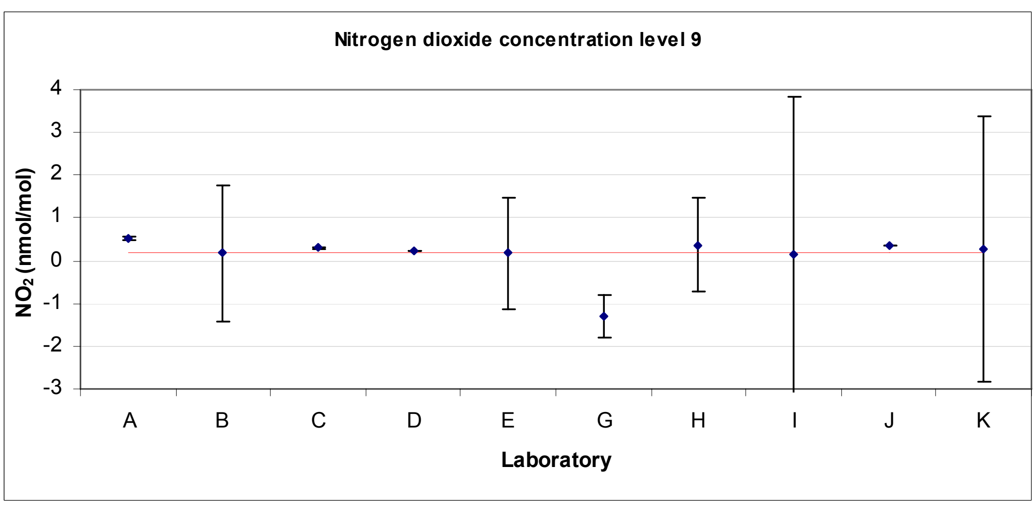

Figure 51: Reported values for NO_2 concentration level 9.

Table 46: Reported values for NO_2 concentration level 10.

parameter: NO2	all units are nmol/mol									
level: 10	x*: 13.61	s*: 0.51								
	A	B	C	D	E	G	H	I	J	K
xi,1	13.50	14.20	13.1	13.5	14.0	12.1	13.9	13.8	13.51	13.1
xi,2	13.50	14.32	13.0	13.7	14.1	12.1	13.9	13.8	13.53	13.3
xi,3	13.50	14.36	13.4	13.7	14.2	12.3	13.9	14.0	13.60	13.3
xi	13.500	14.293	13.17	13.63	14.10	12.17	13.90	13.87	13.547	13.23
si	0.000	0.083	0.21	0.12	0.10	0.12	0.00	0.12	0.047	0.12
u(xi)	0.60	0.83	0.20	0.3	0.2	0.6	0.6	1.7	0.65	1.55
U(xi)	1.20	1.7	0.40	0.7	0.4	1.3	1.3	3.5	1.30	3.1

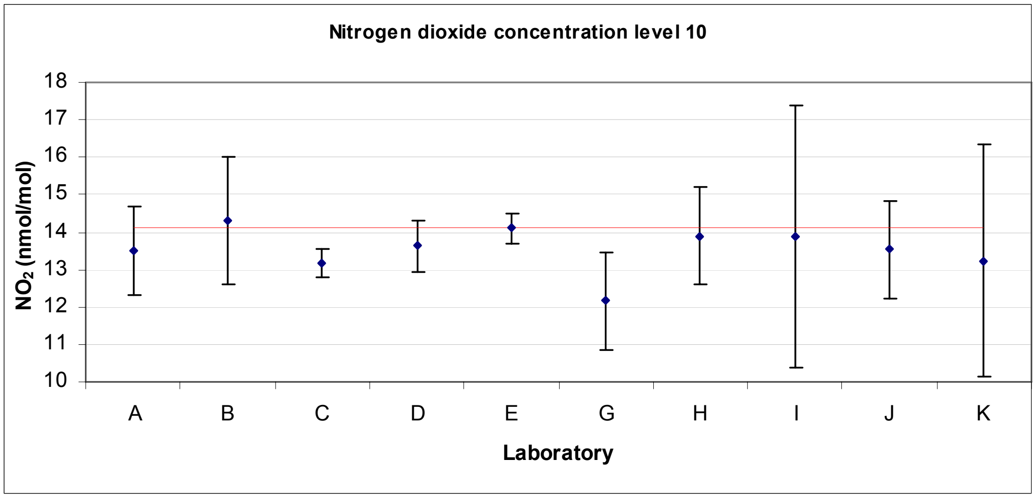

Figure 52: Reported values for NO_2 concentration level 10.

Annex C. Precision of standardized measurement methods

For the main purpose of monitoring trends between different IEs undertaken by ERLAP the precision of standardized SO_2, CO, O_3 and NO_X measurement methods [6], [7], [8] and [9] as implemented by NRLs was evaluated. Applied methodology is described in ISO 5725-1, -2 and -6 [18], [19] and [20]. The precision experiment involved nine laboratories. For O_3, CO and SO_2 six, and NO, NO_2 eleven concentration levels were tested. Data consistency and outlier tests have been performed (Annex D).

The repeatability standard deviation (s_r) was calculated in accordance with ISO 5725-2 as the square root of average within laboratory variance. The repeatability limit (r) is calculated using equation 8 [20]. It represents the biggest difference between two test results found on an identical test gas by one laboratory using the same apparatus within the shortest feasible time interval, that should not been exceeded on average more than once in 20 cases in the normal and correct operation of method.

$$r = t_{95\%,18} \cdot \sqrt{2} \cdot s_r \qquad (8)$$

The reproducibility standard deviation (s_R) was calculated in accordance with ISO 5725-2 as the square root of sum of repeatability and between laboratory variance. The reproducibility limit (R) is calculated using equation 9 [20]. It represents the biggest difference between two measurements on an identical test gas reported by two laboratories, that should not occur on average more than once in 20 cases in the normal and correct operation of method.

$$R = t_{95\%,8} \cdot \sqrt{2} \cdot s_R \qquad (9)$$

The repeatability standard deviation was evaluated with 18 (9·(3-1)) degrees of freedom (ν) and reproducibility standard deviation with 8 (9-1) degrees of freedom. The critical range student factors ($t_{\alpha,\nu}$) are 2,101 and 2,306 respectively.

In Table 47-Table 51 and Figure 53-Figure 57 the repeatability and reproducibility limits of measurement methods are presented with (r, R) and without (r*, R*) outliers. Also presented is ‘reproducibility from common criteria (R(from σ_p))’ calculated by substituting s_R in equation 9 with a ‘standard deviation for proficiency assessment’ (Table 3). Comparison between R and R(from σ_p) serves to indicate that σ_p is realistic ([17] 6.3.1) or from the other point of view, that the general methodology implemented by NRLs is fit for σ_p.

Table 47: The R and r of CO standard measurement method.

CO data (µmol/mol)						
all data			without outliers			
group average	repeatability limit : r	reproducibility limit : R	group average	repeatability limit : r*	reproducibility limit : R*	reproducibility limit (relative)
0.02		0.11	0.00		0.04	
1.01	0.01	0.17	1.01	0.01	0.17	
2.01	0.01	0.33	2.01	0.01	0.33	
4.28	0.03	0.29	4.28	0.03	0.29	
5.99	0.07	0.49	5.99	0.07	0.49	
8.54	0.02	0.62	8.54	0.02	0.62	7.3%

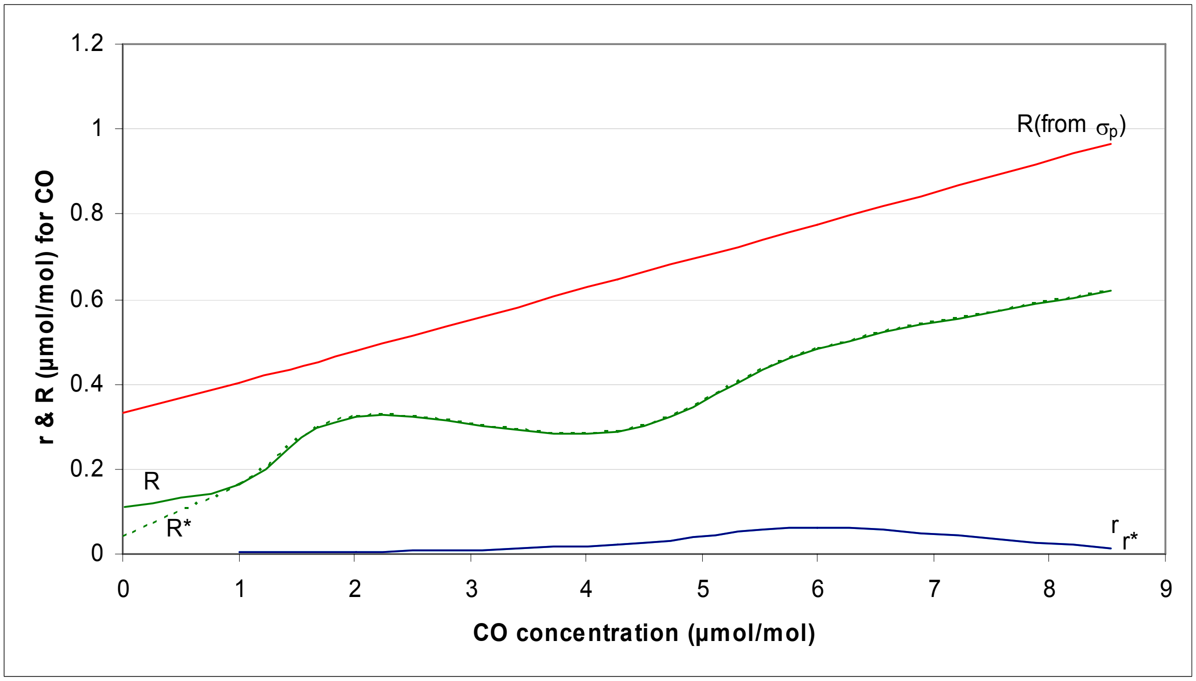

Figure 53: The R and r of CO standard measurement method as a function of concentration.

Table 48: The R and r of O_3 standard measurement method.

O3 data (nmol/mol)						
all data			without outliers			
group average	repeatability limit : r	reproducibility limit : R	group average	repeatability limit : r*	reproducibility limit : R*	reproducibility limit (relative)
0.2		1.5	0.1		1	
14.8	0.2	2.4	14.5	0.2	1.7	
22.5	0.2	3	22.1	0.3	1.7	
60.9	0.2	6	60.1	0.3	2.3	
101.7	1	9.4	100.3	0.9	3.3	
117.7	1.5	10.4	116.1	1.5	3.5	3.0%

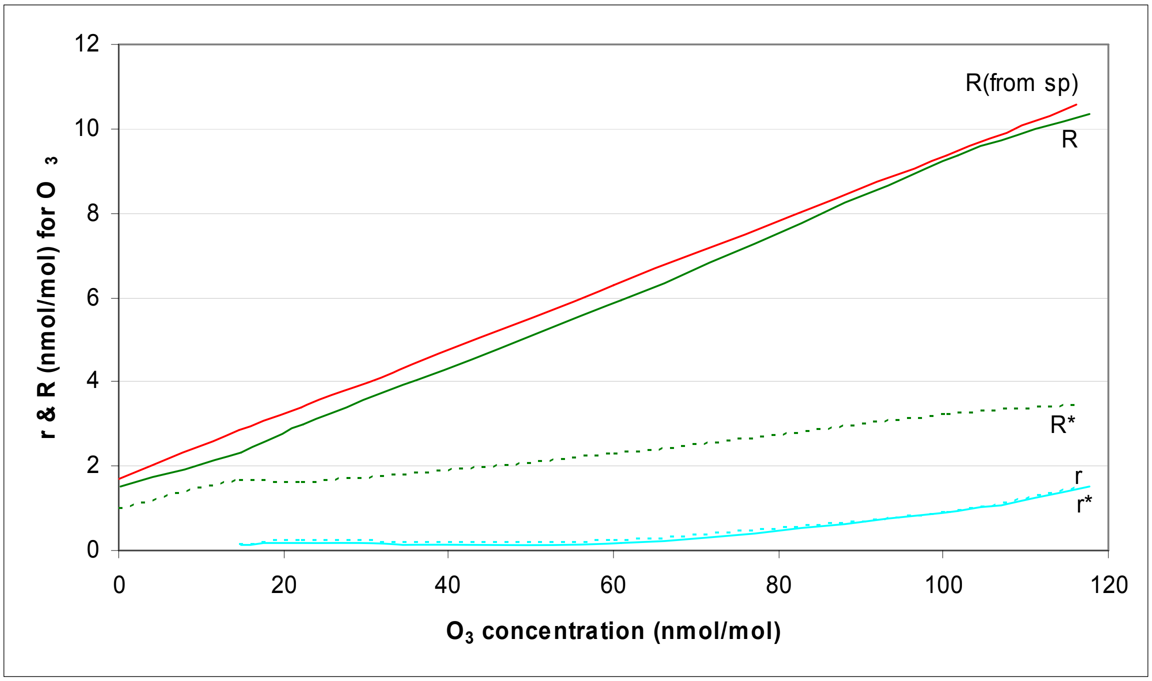

Figure 54: The R and r of O_3 standard measurement method as a function of concentration.

Table 49: The R and r of SO_2 standard measurement method.

SO2 data (nmol/mol)						
all data			without outliers			
group average	repeatability limit : r	reproducibility limit : R	group average	repeatability limit : r*	reproducibility limit : R*	reproducibility limit (relative)
0.1		0.7	0.1		0.7	
3.1	0.3	0.9	3.1	0.3	1	
7.6	0.2	1.3	7.5	0.2	1.2	
18.1	0.6	3.6	17.8	0.2	1.8	
46.6	0.3	5.2	46.2	0.3	3.5	
131.9	0.5	12.1	131.0	0.5	9.3	7.1%

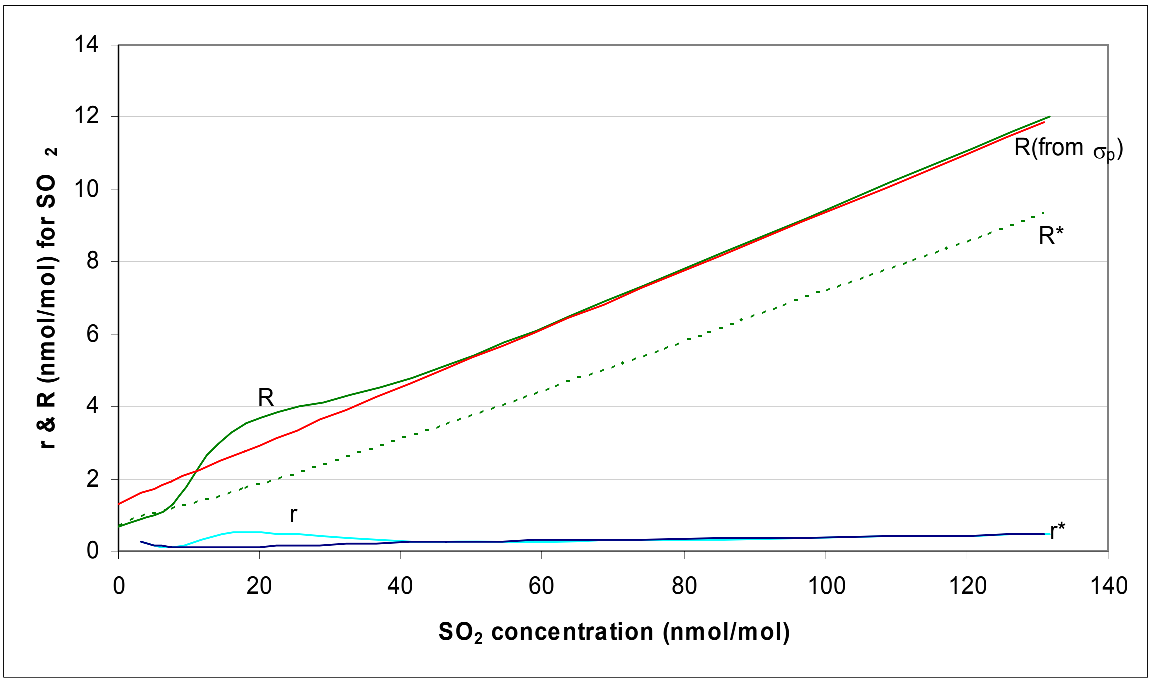

Figure 55: The R and r of SO_2 standard measurement method as a function of concentration.

Table 50: The R and r of NO standard measurement method.

NO data (nmol/mol)			
all data			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.1		0.8	
1.7	0.3	1	
15.2	1.2	1.8	
28.3	0.4	2.1	
50.1	0.2	3.4	
90.1	0.5	5.2	
150.3	0.9	8.3	
151.2	0.4	8.8	
251.2	1.8	14.3	
385.3	0.9	23.1	
504.9	1.4	30.8	6.1%

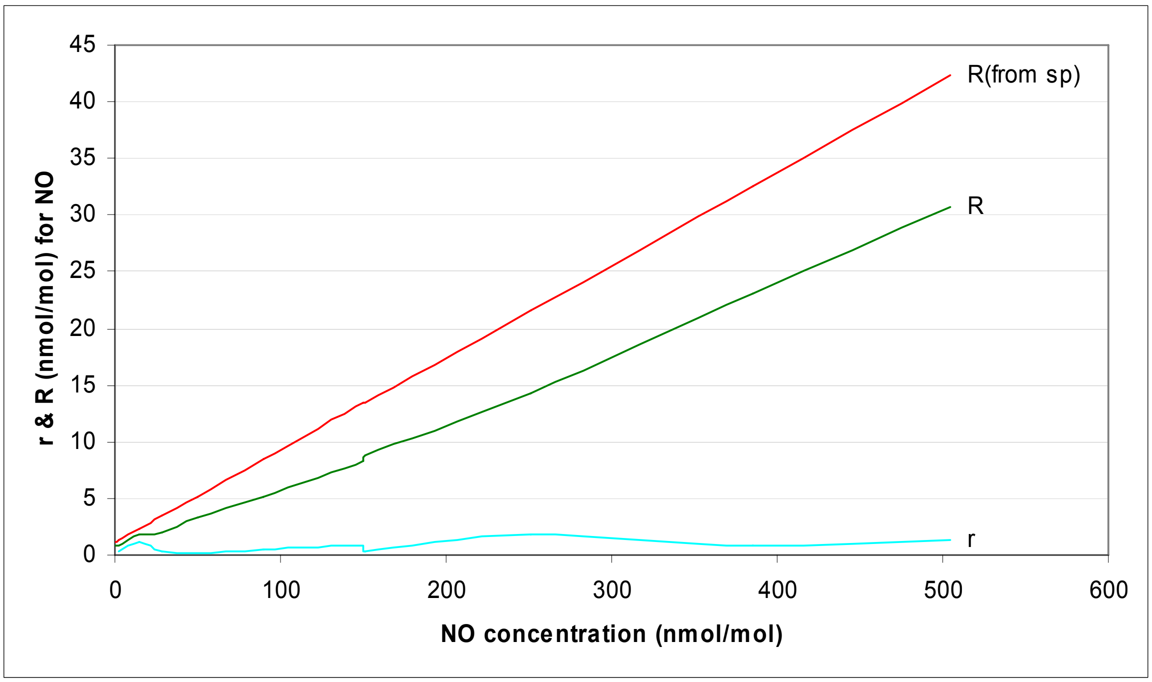

Figure 56: The R and r of NO standard measurement method as a function of concentration.

The reproducibility and repeatability of NO_2 measurements are dependant on both NO and NO_2 concentrations. In Table 51 both concentrations are given and in Figure 57 R and r are plotted as functions of NO_2 concentration.

Table 51: The R and r of NO_2 standard measurement method.

NO2 data (nmol/mol)								
all data				without outliers				
NO	NO2	NO2		NO	NO2	NO2		
group average	group average	repeatability limit : r	reproducibility limit : R	group average	group average	repeatability limit : r*	reproducibility limit : R*	reproducibility limit (relative)
0.1	-0.1		1.9	0.1	0.1		0.4	
1.7	13.6	0.3	2.1	1.7	13.6	0.3	2.1	
15.2	0.1	0.5	1.9	15.2	0.3	0.5	0.6	
28.3	21.9	0.3	2.0	28.3	21.9	0.3	2.0	
50.1	0.2	0.2	1.5	50.1	0.2	0.2	1.5	
90.1	60.5	0.6	4.0	90.1	60.5	0.6	4.0	
150.3	0.5	0.3	1.6	150.3	0.5	0.3	1.6	
151.2	101.5	0.7	7.4	151.2	101.5	0.7	7.4	
251.2	1.5	0.7	3.5	251.2	1.5	0.7	3.5	
385.3	119.8	1.4	14.1	385.3	119.8	1.4	14.1	11.8%
504.9	1.8	0.9	6.9	504.9	1.8	0.9	6.9	

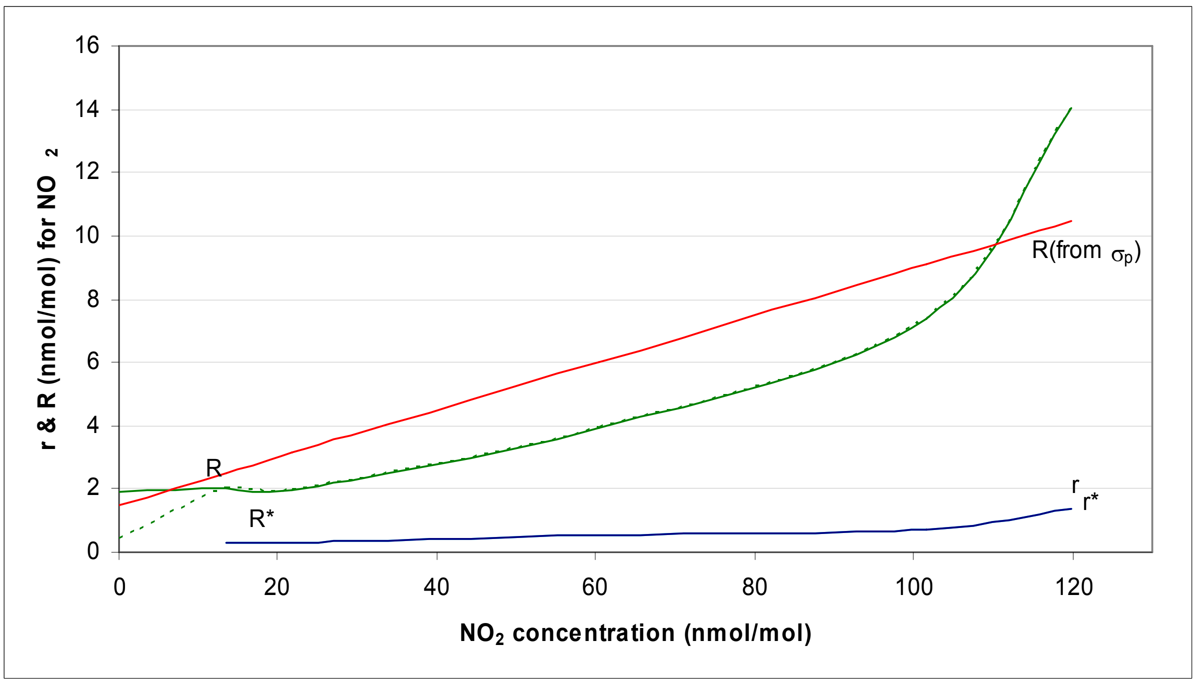

Figure 57: The R and r of NO_2 standard measurement method as a function of NO_2 concentration.

Annex D. Scrutiny of results for consistency and outliers

The precision evaluation (Annex C) focuses on data that are as much as possible the reflection of every day work of NRLs and thus represents the comparability of participant's standard operating procedures. For that reason a procedure for the detection of exceptional errors (error during typing, slip in performing the measurement or calculation, the bad averaging interval, malfunction of instrumentation, etc.) was applied. In this procedure the IE data first underwent the scrutiny for its consistency and the detection of statistical outliers as described in ISO 5725-2. Then the six laboratories showing some form of statistical inconsistency were contacted to try to ascertain the cause of discrepancies. Laboratories were allowed to correct their results and four did so. After that data was considered of appropriate quality and the final tests of statistical outliers were performed.
In this final test "Grubb's one outlying observation test" was performed Figure 58 to Figure 62. For runs:

a.) where outliers were detected outliers were removed and "Grubb's one outlying observation test" was repeated. After this one repetition there were no more outliers in these runs.
b.) where no outliers were detected the "Grubb's two outlying observations test" was performed (Figure 63 to Figure 67).

Statistical outliers obtained at this stage are not considered as due to extraordinary errors but due to significant difference in participant's standard operating procedure. These "genuine" statistical outliers are presented in table below:

Table 52: "Genuine" statistical outliers.

Parameter	Run	Participant	Failing test
SO2	3	A	"Grubb's one outlying observation test" (Figure 58)
CO	0	A	"Grubb's one outlying observation test" (Figure 59)
NO2	0	G	"Grubb's one outlying observation test" (Figure 62)
NO2	9	G	"Grubb's one outlying observation test" (Figure 62)
O3	1	A & G	"Grubb's two outlying observations test" (Figure 65)
O3	2	A & G	"Grubb's two outlying observations test" (Figure 65)

Not to have unrealistic jumps in the evaluation of precision of standardized method all SO_2 data of participant A and all O_3 data of participants A and G were removed from this evaluation.

Presented in the following figures are Grubb's one outlying observation test statistics for the minimum (blue) and maximum (orange with pattern) values of each run. Values between the two lines are considered strugglers and values over violet line are considered outliers.

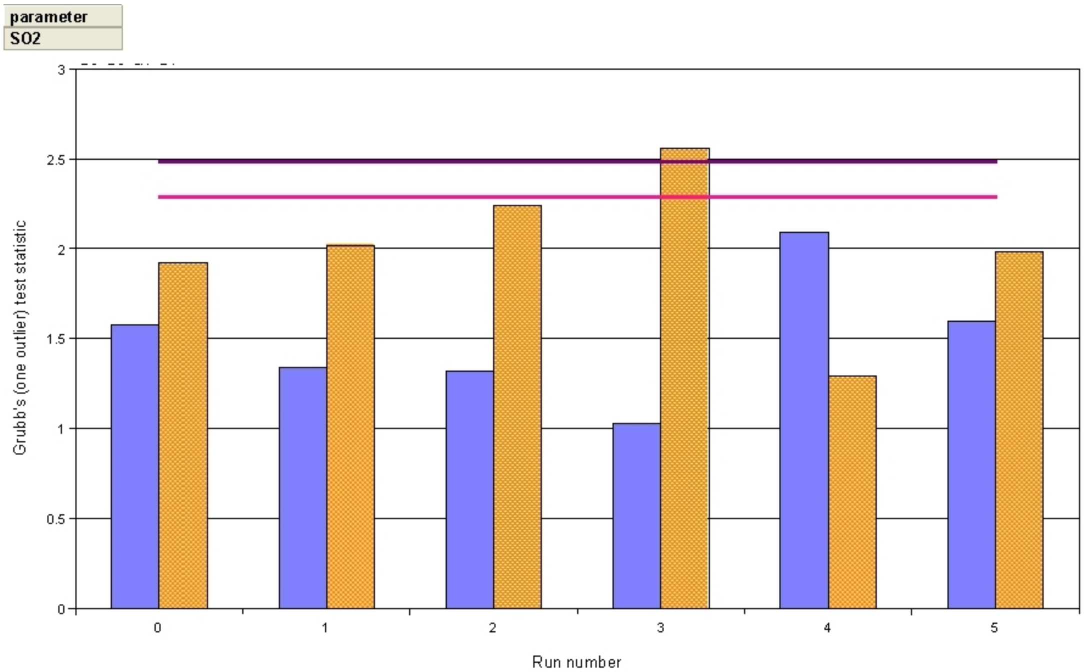

Figure 58: Grubb's one outlying observation test statistics for SO_2 runs.

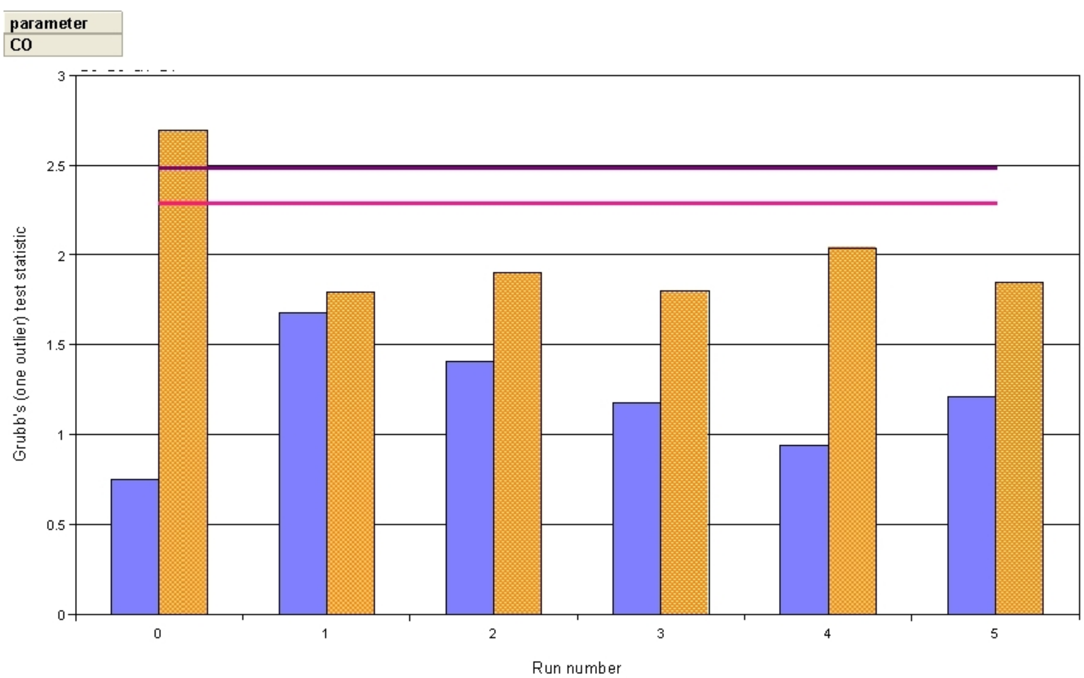

Figure 59: Grubb's one outlying observation test statistics for CO runs.

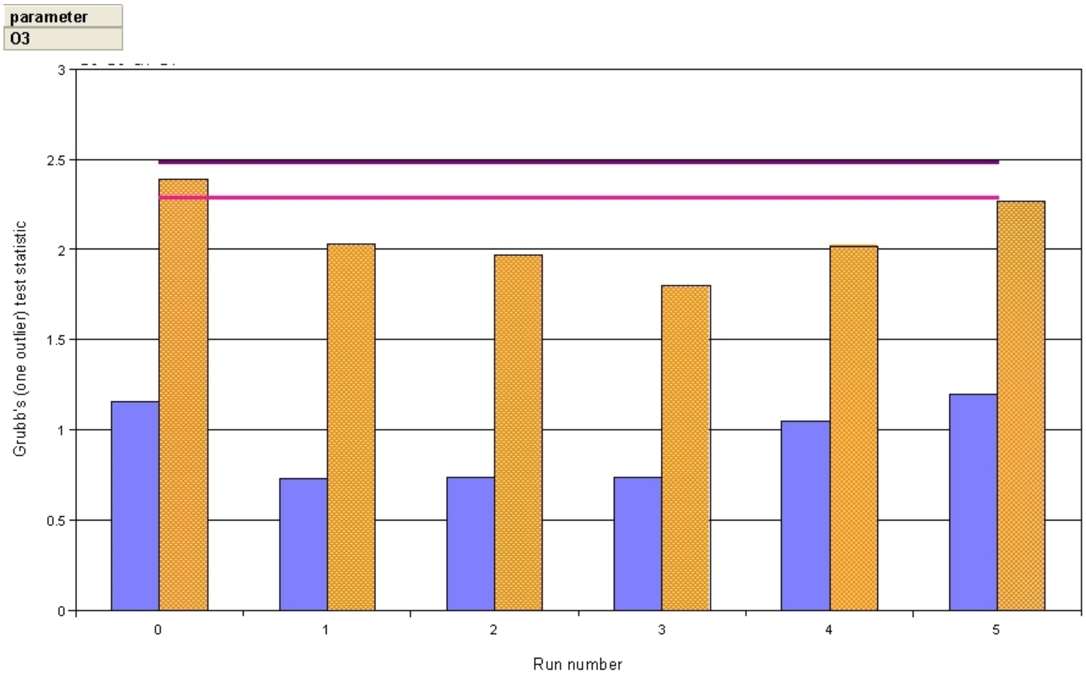

Figure 60: Grubb's one outlying observation test statistics for O_3 runs.

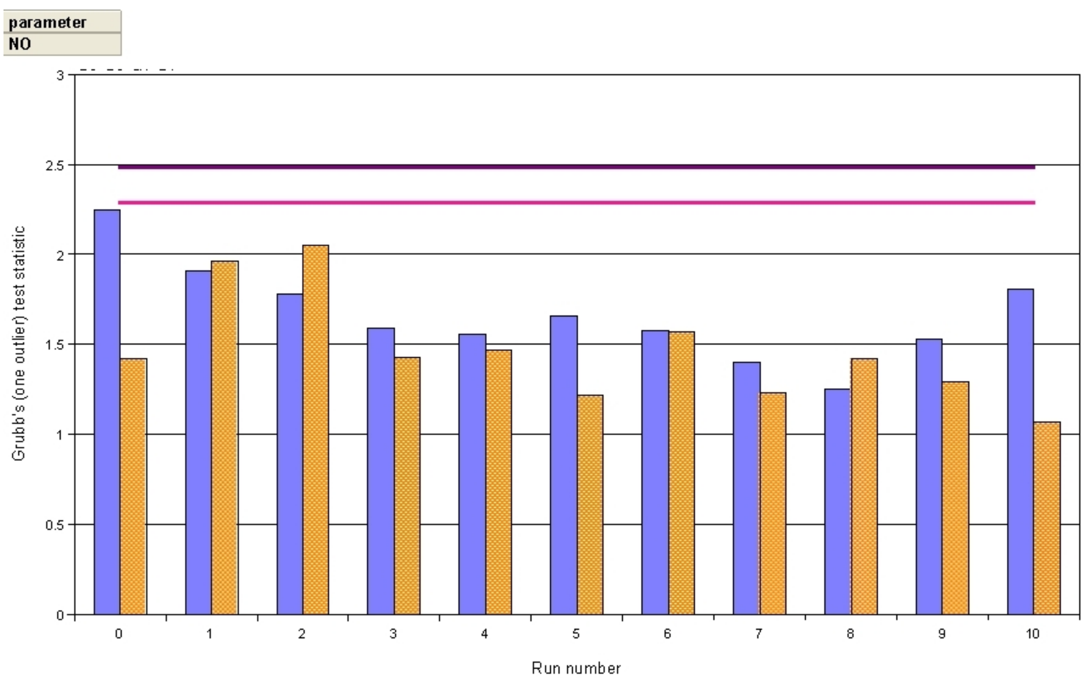

Figure 61: Grubb's one outlying observation test statistics for NO runs.

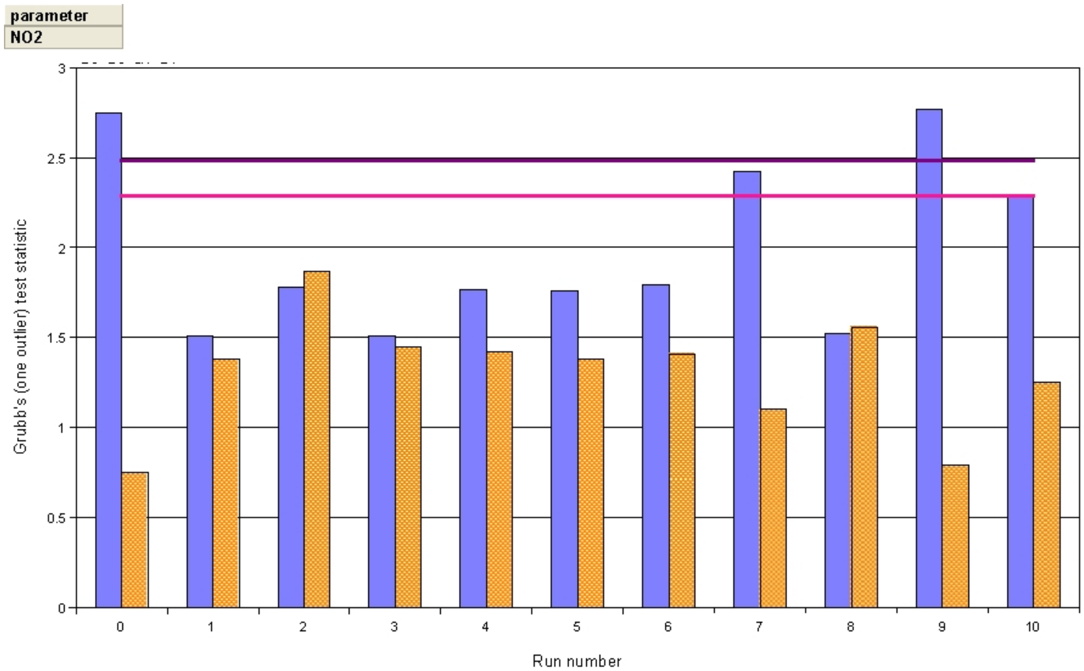

Figure 62: Grubb's one outlying observation test statistics for NO_2 runs.

Grubb's two outlying observations test statistics for the minimum (blue) and maximum (orange with pattern) values of all runs that passed "Grubb's one outlying observation" test. Values between the two lines are considered strugglers and values under red line are considered outliers.

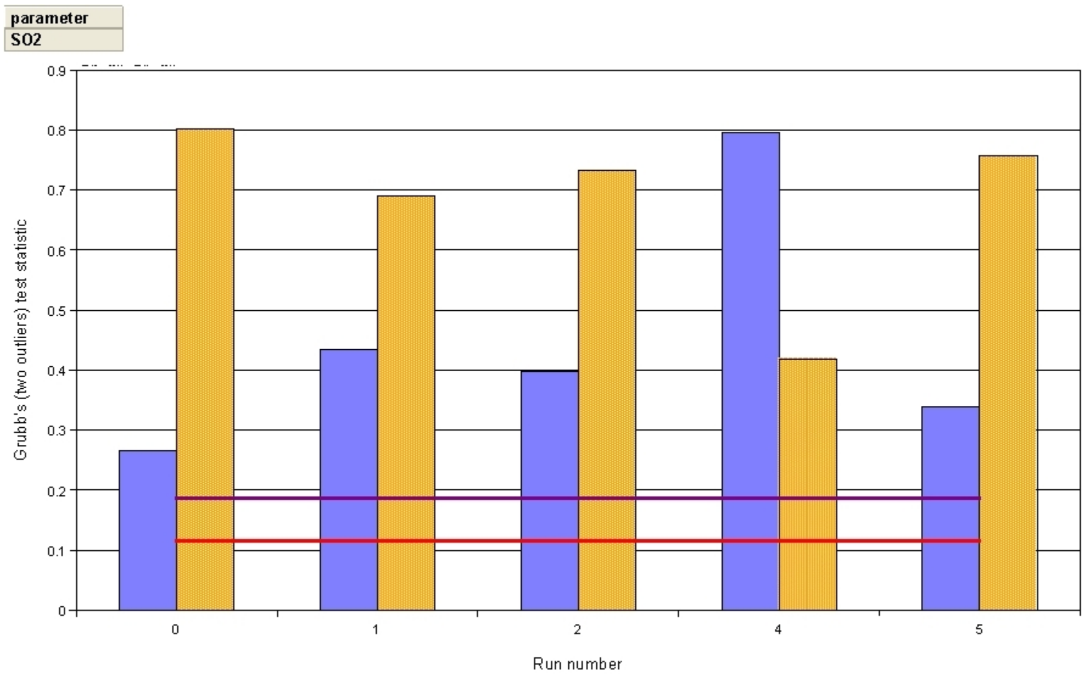

Figure 63: Grubb's two outlying observations test statistics for SO_2 runs

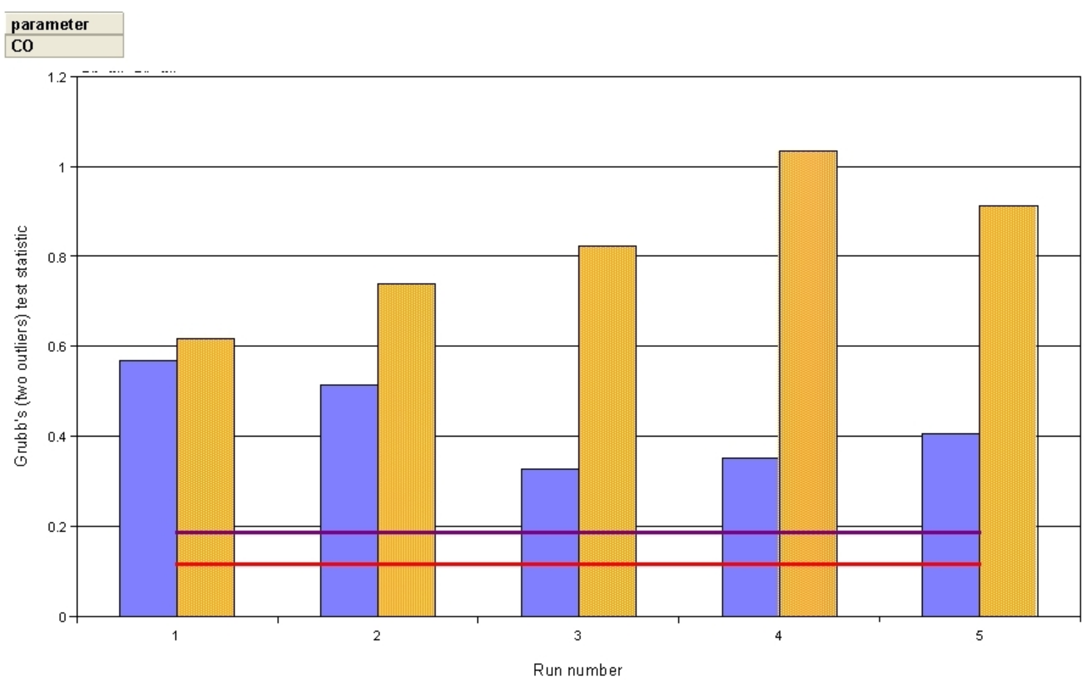

Figure 64: Grubb's two outlying observations test statistics for CO runs

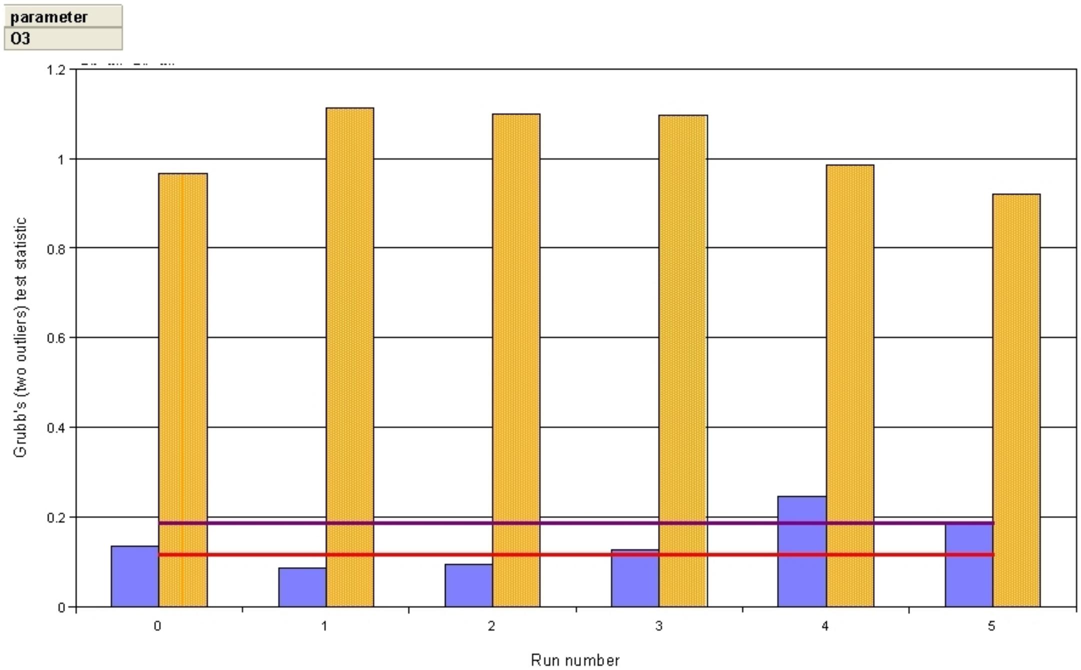

Figure 65: Grubb's two outlying observations test statistics for O3 runs

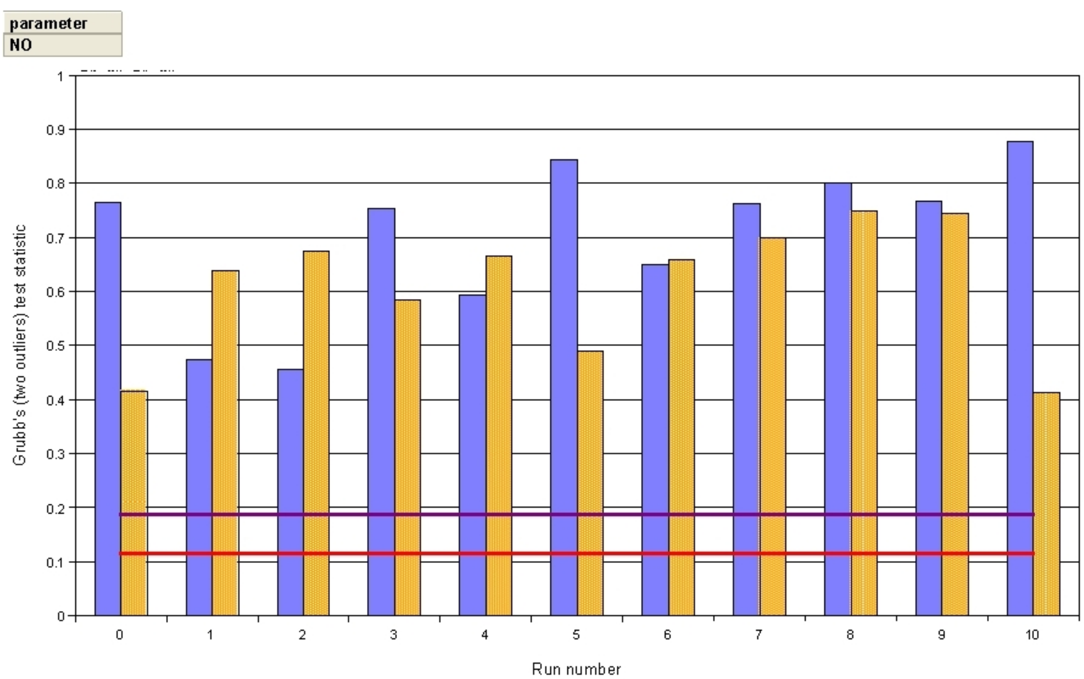

Figure 66: Grubb's two outlying observations test statistics for NO runs

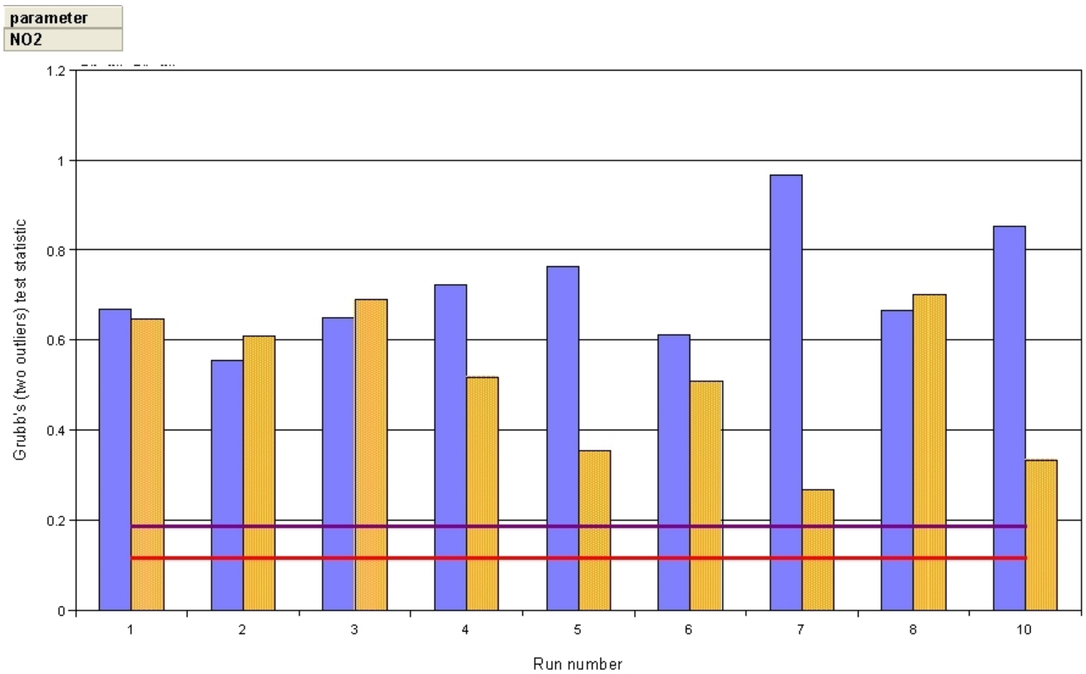

Figure 67: Grubb's two outlying observations test statistics for NO_2 runs

European Commission

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Abstract
In June 2007 in Ispra (IT), 9 AQUILA (Network of European Air Quality Reference Laboratories) laboratories and one laboratory of the World Health Organisations (WHO) Euro-Region met at an intercomparison exercise to evaluate their proficiency in the analysis of inorganic gaseous pollutants covered by European Air Quality Directives (SO_2, CO, NO, NO_2 and O_3).

The proficiency evaluation, where each participant's bias was compared to two criteria, provides information on the current situation and capabilities to the European Commission and can be used by participants in their quality control system.

In terms of criteria imposed by the European Commission, 60% of the results reported by AQUILA laboratories were good both in terms of measured values and reported uncertainties. Another 37% of the results had good measured values, but the reported uncertainties were either too small (4%) or too high (33%).

The comparability of results among AQUILA participants is satisfactory for O_3, SO_2, CO and NO measurement method, but the pollutant NO_2 needs further improvements and harmonization programmes.

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